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LOUIS P. HAMMETT, PH.D , *Consulting Editor*

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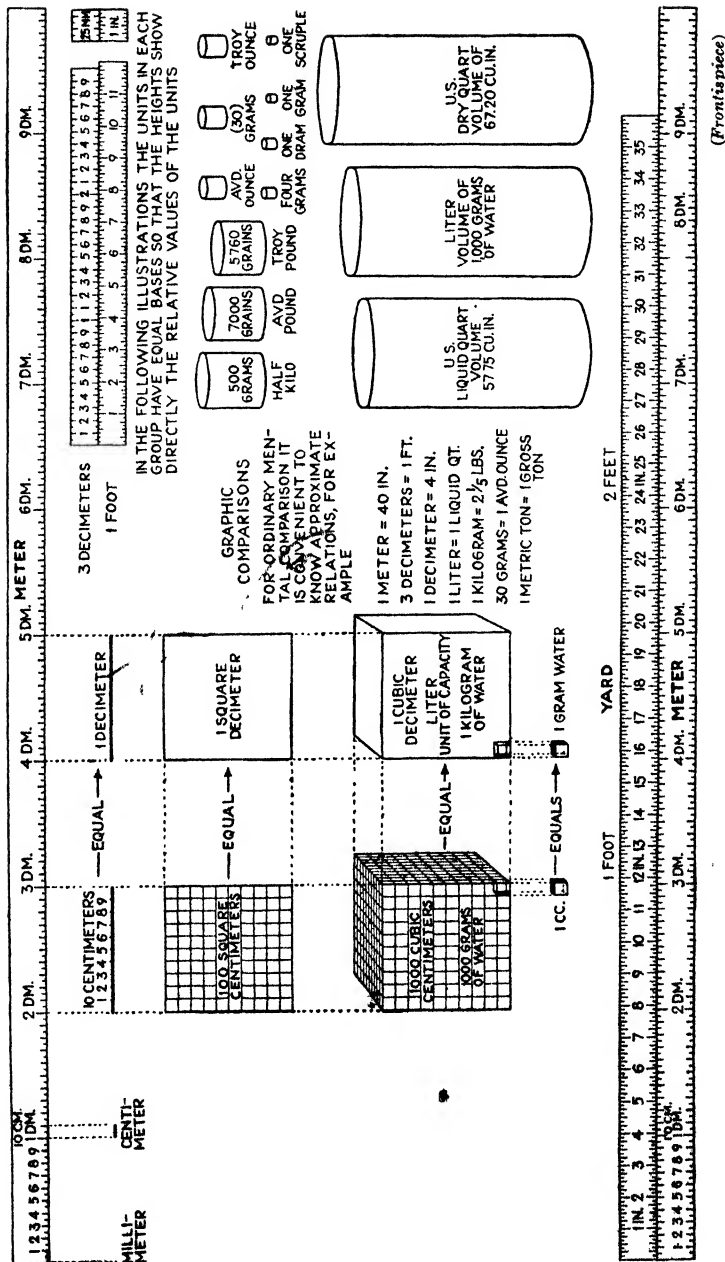
CHEMICAL CALCULATIONS

A SELECTION OF TITLES FROM THE INTERNATIONAL CHEMICAL SERIES

LOUIS P. HAMMETT, PH.D., *Consulting Editor*

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CHEMICAL CALCULATIONS

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Fourth Edition

FOURTH IMPRESSION

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CHEMICAL CALCULATIONS

CHAPTER I

OUTLINE

MEASURES AND WEIGHTS.

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2. Absolute zero.
3. Absolute temperature.

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Relative density.

Vapor density.

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Specific gravity.

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2. Body heavier than water. Insoluble in water.
3. Body heavier than water. Soluble in water.
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MEASURES AND WEIGHTS

In the scientific world a uniform method of expressing measures and weights has been established. This organization for

measures and weights is the metric system, in which the units are not only interrelated but definite and fixed.

Length.—The fundamental unit of length is the **meter** (m.) which is divided into 100 equal parts, called **centimeters** (cm.). A centimeter is further subdivided into **millimeters** (mm.) such that 1 cm. equals 10 mm. or 1 mm. is 0.1 cm.

For purposes of measuring still smaller unit lengths, various submultiples of the meter are used. For convenience in expressing small entities such as the dimensions of colloidal particles, wave length of light (visible, ultraviolet, X rays, γ rays, cosmic rays), or atomic or ionic distances, the following units of length are employed: the micron (μ), millimicron¹ ($m\mu$), angstrom (A.), the X unit (X.U.). These units are included in Table I to show concisely the actual relationship between each unit and the centimeter.

TABLE I.—LENGTH

Unit length	Symbol	Expressed in centimeters
1 kilometer.....	km.	100,000 cm. (1,000 m.)
1 meter.....	m.	100 cm.
1 decimeter.....	dm.	10 cm.
1 centimeter.....	cm.	1 cm.
1 millimeter.....	mm.	0.1 cm.
1 micron.....	μ .	0.0001 cm. (10^{-4} cm.)
1 millimicron.....	$m\mu$.	0.0000001 cm. (10^{-7} cm.)
1 angstrom.....	A. or A.U.	0.00000001 cm. (10^{-8} cm.)
1 X unit.....	X.U.	0.00000000001 cm. (10^{-11} cm.)

Volume.—The unit of volume is the **cubic centimeter** (cc.), which is the volume of a cube of inside edge 1 cm. in length. A still larger unit of volume is the **liter** (l.), which is defined as the volume occupied by 1 kg. of water at 4°C. (the temperature of maximum density of water) and corresponds to 1,000.027 cc. The U. S. Bureau of Standards proposes the adoption of the **milliliter** (ml.) on the basis of the fact that 1 l. contains 1,000 ml.

¹ The prefix "micro-" denotes "millionth"; the prefix "milli-" denotes "thousandth." Thus, 1 micron (μ) = 1 millionth meter = $\frac{1}{1,000,000}$ m. = 10^{-6} m. = 10^{-4} cm. = 10^{-3} mm. (0.001 mm.). Also, 1 millimicron ($m\mu$) = 1 one-thousandth micron = $1/10^3 \times 10^{-4}$ cm. = 10^{-7} cm. = 10 A.

For practical purposes the **cubic centimeter** and the **milliliter** can be considered the same and thus used interchangeably in chemical calculations. Throughout this text the authors have retained the cubic centimeter as the fundamental unit of volume, since it is in common usage in the modern textbooks of Chemistry, the *Journal of the American Chemical Society*, and various other publications.

TABLE II.—VOLUME

1 liter (l.) = 1,000 milliliters (ml.)

1 liter (l.) = 1,000.027 cubic centimeters (cc.)

Weight.—The unit of weight is the **gram** (g.), which is the weight of 1 cc. of water at 4°C. The temperature at which water has its maximum density is 4°C. At this temperature the density of water is 1, or 1 cc. of water weighs 1 g. at 4°C. Above and below 4°C. the density of water is less than 1. Water at this temperature is the standard selected in the determination of the density of liquids and solids. The subject of density will be considered in greater detail later on in this chapter. A larger unit of weight is the **kilogram** (kg.), equal to 1,000 g. Thus 1,000 cc., or 1 l., of water weighs 1 kg. A unit smaller than the gram is known as the **milligram** (mg.) and is one one-thousandth part of a gram (1 mg. = 0.001 g.), or 1,000 mg. corresponds to 1 g., or 0.2 g. is 200 mg.

TABLE III.—WEIGHT (MASS)

Unit weight	Symbol	Expressed in grams	Expressed in milligrams
1 kilogram.....	kg.	1,000 g.	1,000,000 mg.
1 gram.....	g.	1 g.	1,000 mg.
1 decigram.....	dg.	0.1 g.	100 mg.
1 centigram.....	cg.	0.01 g.	10 mg.
1 milligram.....	mg.	0.001 g.	1 mg.

The system of measures and weights in common use in everyday life in the United States of America and conveniently referred to in this text as the "U. S. A." system is made up of units that are definitely not interrelated. The result of this nonconformity in the system makes for distinct confusion; in many instances

it is not conveniently applicable; and at best it is cumbersome to deal with. This is especially true in the measurement of wave lengths of light or sound and the weighing of extremely minute quantities which workers in the sciences are compelled to make in the laboratory at all times.

TABLE IV.—SOME COMMON UNIT MEASURES AND WEIGHTS
(A) Conversion of U. S. A. System to Metric System

Length	Cubic
1 inch (in.) = 2.54 cm. = 25.4 mm.	1 cu. in. = 16.387 cc.
1 foot (ft.) = 0.3048 m. = 30.48 cm.	1 cu. ft. = 28.31 liters (l.)
1 mile (mi.) = 1.609 km.	
Capacity	Weight
1 fluid dram = 3.70 ml. or cc.	1 grain (gr.) = 64.7989 mg.
1 fluid ounce (fl. oz.) = 29.57 ml. or cc.	1 oz. (avoirdupois) = 28.35 g.
1 fluid quart (fl. qt.) = 0.9463 l.	1 lb. (avoirdupois) = 453.59 g.
1 gallon (U. S. A.) = 3.7853 l.	1 oz. (Troy) = 31.1034 g.

(B) Conversion of Metric System to U. S. A. System

Length	Cubic
1 meter (m.) = 39.370 in. = 3.2808 ft. = 1.0936 yds.	1 cubic centimeter (cc. or ml.) = 0.061 cu. in.
1 kilometer (km.) = 0.62137 mile (mi.)	1 cubic meter (cu. m.) = 35.314 cu. ft.
Capacity	Weight
1 liter (1,000 cc. or ml.) = 1.0567 qt.	1 milligram (mg.) = 0.0154 grain
1 decaliter (10 l.) = 2.6418 gal.	1 kilogram (1,000 g.) = 2.2046 lb. (avoirdupois)

In spite of the many inconveniences of the U. S. A. system and the efforts on the part of groups of eminent scientists in the United States to bring about in industry and commerce a wholesale conversion to the metric system—with all its attendant simplicity and advantages—the fact remains that a *laissez-faire* attitude prevails. Therefore it becomes necessary for the

scientific-minded student and worker to familiarize himself with both systems of weights and measures.

It is frequently necessary to make conversions from the U. S. A. system of units to the metric system, and vice versa. Some of the common units and their conversions are given in Table IV. For a more comprehensive table of conversion factors, the reader is referred to the Appendix Table I (page 251).

TABLE V.—CONVENIENT WEIGHT CONVERSIONS

Weight (mass).....	Grams	Ounces (avoir.)	Pounds (avoir.)	Kilograms
Symbol.....	g.	oz.	lb.	kg.
Grams.....	1.0	0.03527	0.00220	0.001
Ounces (avoir.).....	28.3495	1.0	0.0625	0.028349
Pounds (avoir.).....	453.59	16.0	1.0	0.45359
Kilograms.....	1,000.0	35.274	2.2046	1.0

TABLE VI.—CONVENIENT CAPACITY CONVERSIONS

Capacity ...	Fluid ounces	Pints	Quarts	Gallons	Cubic centi- meters	Liter
Symbol.....	fl. oz.	pt.	qt.	gal.	cc.	l.
Fluid ounces	1.0	0.0625	0.03125	0.0078125	29.5737	0.029573
Pints.....	16.0	1.0	0.5	0.125	473.15	0.47315
Quarts.....	32.0	2.0	1.0	0.25	946.3	0.9463
Gallons.....	128.0	8.0	4.0	1.0	3785.3	3.7853
Cubic centi- meters ...	0.033815	0.002113	0.001056	0.000264	1.0	0.001
Liters.....	33.8147	2.1134	1.0567	0.2642	1000.0	1.0

THE MEASUREMENT OF TEMPERATURE

The temperature of a body specifies its state with respect to its ability to transfer heat to other bodies and is usually expressed in degrees on one of the four scales: (a) centigrade; (b) Fahrenheit; (c) absolute; (d) Réaumur.

Comparison of the four scales may be made by considering on each the freezing point and boiling point of pure water, as follows:

SCALE	FREEZING POINT OF PURE WATER	BOILING POINT OF PURE WATER
Centigrade.....	0°	100°
Fahrenheit.....	32°	212°
Absolute { Kelvin.....	273°	373°
{ Rankine.....	492°	672°
Réaumur.....	0°	80°

The Fahrenheit scale (°F.) is in common use in our domestic life. The centigrade (°C.) and the absolute (°A.) scales are used almost exclusively in the scientific world.

A comparison of the two most commonly used thermometric scales, *i.e.*, Fahrenheit and centigrade, may be made by con-

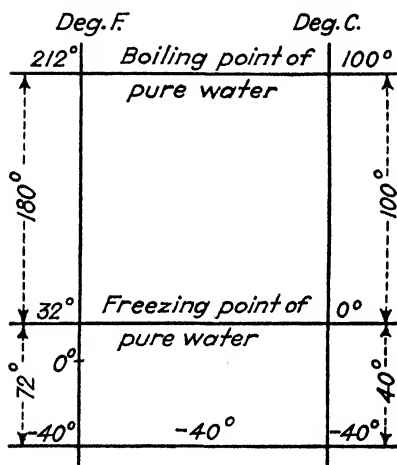


FIG. 1.

sidering the freezing point (f.p.) and the boiling point (b.p.) of pure water on each scale, as shown graphically in Fig. 1.

Between the freezing point and boiling point of pure water there are 100 centigrade degrees, or 180 Fahrenheit degrees; hence,

$$1^{\circ}\text{C.} = \frac{180}{100} = \frac{9}{5}^{\circ}\text{F.}$$

$$1^{\circ}\text{F.} = \frac{100}{180} = \frac{5}{9}^{\circ}\text{C.}$$

The ratio of the differences between the freezing point and the boiling point of water on the centigrade and Fahrenheit

scales can be expressed by the formula

$$\begin{aligned}\frac{^{\circ}\text{C.}}{^{\circ}\text{F.} - 32} &= \frac{100}{180} = \frac{5}{9} \\ ^{\circ}\text{C.} &= \frac{5}{9} (^{\circ}\text{F.} - 32) \\ ^{\circ}\text{F.} &= \frac{9}{5} (^{\circ}\text{C.}) + 32\end{aligned}$$

To some workers the use of these formulas is considered an inconvenience, and a simplification of the method of conversion from one temperature scale to the other has been suggested,¹ based on the following: (a) that the relative magnitude of the two kinds of degrees is in the ratio of 9:5 and (b) that the number

¹ Shaw, H. G. *J. Chem. Educ.*, **8**, 729 (1931).

-40° expresses the same temperature on both scales. Figure 1 shows the three equivalent points on each of the two thermometric scales. It should be noted that the ratios of the degree-distance between these points $^{\circ}\text{F}.:^{\circ}\text{C}.$ (*i.e.*, 180:100 and 72:40), reduced to lowest terms, are 9:5. The simplification rule follows: (a) To the given temperature add 40; (b) multiply this sum by $\frac{5}{9}$ or $\frac{9}{5}$; (c) from this product subtract 40. The remainder is the temperature expressed in the other scale. The proper fraction is readily selected if one realizes that there are more degrees Fahrenheit than degrees centigrade for a given interval. Thus, in converting degrees centigrade to degrees Fahrenheit the fraction is $\frac{9}{5}$; and, vice versa, from degrees Fahrenheit to degrees centigrade the fraction is $\frac{5}{9}$.

Expressed mathematically, the relation becomes

$$\frac{^{\circ}\text{F.} + 40}{180} = \frac{^{\circ}\text{C.} + 40}{100}$$

or

$$\frac{^{\circ}\text{F.} + 40}{9} = \frac{^{\circ}\text{C.} + 40}{5}$$

Example.—What temperature on the centigrade scale corresponds to $120^{\circ}\text{F}.$?

A. Solving by ordinary methods:

$120^{\circ}\text{F}.$ is $120 - 32$, or 88 Fahrenheit degrees above the freezing point of pure water.

$$88^{\circ}\text{F.} = \frac{5}{9} \times 88 = 48.8^{\circ}\text{C.}$$

B. Solving by the foregoing rule.

$$\frac{120 + 40}{9} = \frac{^{\circ}\text{C.} + 40}{5}$$

$$^{\circ}\text{C.} = (120 + 40)\frac{5}{9} - 40 = 48.8^{\circ}$$

Therefore, 48.8°C. corresponds to $120^{\circ}\text{F}.$

ABSOLUTE ZERO

It is a familiar fact that when a definite quantity of gas is subjected to an increase in temperature (at constant pressure), the volume will increase; and that if the temperature is lowered

(at constant pressure), the volume will decrease. With a given volume of a gas at 0°C. , experiment shows that it expands approximately $\frac{1}{273}$ of its volume at 0°C. for each degree centigrade that it is heated. Thus, if we have 273 cc. of gas at 0°C. and increase the temperature to 100°C. (at constant pressure), the volume will increase $\frac{100}{273}$ of its volume at 0°C. , or $273 + (\frac{100}{273} \times 273) = 373$ cc. Also, if we start with 273 cc. of gas at 0°C. and it is cooled to -100°C. (at constant pressure), the volume will be decreased by $\frac{1}{273}$ for each degree that it is cooled; i.e., $273 - (\frac{100}{273} \times 273) = 173$ cc. Again, if we have

$^{\circ}\text{R.}$	$^{\circ}\text{F.}$	$^{\circ}\text{C.}$	$^{\circ}\text{A.}$	Volume
672°	212°	100°	373°	373 cc.
636°	176°	80°	353°	353 cc.
492°	32°	0°	273°	273 cc.
460°	0°	-17.8°	255.2°	255.2 cc.
420°	-40°	-40°	233°	233 cc.
0°	-460°	-273°	0°	0 cc.

FIG. 2.—Equivalent points on thermometric scales.

273 cc. of gas at 0°C. and could lower the temperature to -273°C. it is obvious that the volume, theoretically, would become zero, and the gas should disappear. This point (-273°C.) on the centigrade scale is called the **absolute zero**. Figure 2 shows the relationship between the volume and temperature changes (at constant pressure) when 273 cc. of a gas is confined at 0°C. This, of course, leads directly to the well-known law of Charles, which states that with pressure remaining constant, the volume of a gas is directly proportional to the absolute temperature (Kelvin).

All gases liquefy before the temperature of -273°C. is reached, and the volume then becomes the volume of the substance in

the liquid state. This is small and changes only slightly with further decrease in temperature.

It is of interest to note that Onnes, in working with liquid helium, reached a temperature of 0.82° above absolute zero.

ABSOLUTE TEMPERATURE

Two methods are now employed to express temperatures on the absolute scale: (a) The Kelvin scale ($^{\circ}\text{A.}$), commonly referred to as the absolute scale, in which 0°C. corresponds to 273.16°A. ; and (b) the Rankine scale ($^{\circ}\text{R.}$), in which 0°F. corresponds to 460°R. The **Kelvin scale**, or thermodynamic scale, of temperature is the **absolute centigrade scale**; and the **Rankine scale** of temperature is the **absolute Fahrenheit scale**.

Thus, $32^{\circ}\text{F.} = 0^{\circ}\text{C.} = 273^{\circ}\text{A.} = 492^{\circ}\text{R.}$ (see Fig. 2).

To convert degrees centigrade to degrees absolute (Kelvin), it is necessary only to add 273°C. or

$$t^{\circ}\text{C.} = (t^{\circ}\text{C.} + 273)^{\circ}\text{A.}$$

To convert degrees Fahrenheit to degrees absolute (Rankine), one needs only to add 460°R. , or

$$t^{\circ}\text{F.} = (t^{\circ}\text{F.} + 460)^{\circ}\text{R.}$$

Example.—Convert 68°C. to (a) $^{\circ}\text{A.}$; (b) $^{\circ}\text{R.}$

(a) 68°C. is 68 centigrade degrees above the freezing point of pure water. The absolute zero (Kelvin) is 273 centigrade degrees below the freezing point of pure water; hence 68°C. is $68^{\circ} + 273^{\circ}$, or 341°A.

(b) 68°C. corresponds to 154.4°F. Thus, 154.4°F. is 154.4 minus 32, or 122.4° above the freezing point of pure water. The absolute zero (Rankine) is $(460^{\circ} + 32^{\circ})$, or 492° below the freezing point of pure water. Hence 154.4°F. corresponds to $122.4^{\circ} + 492^{\circ} = 614.4^{\circ}\text{R.}$ Or 154.4°F. is 154.4 Fahrenheit degrees above 0°F. The absolute zero (Rankine) is 460° below 0°F. So 154.4°F. corresponds to $(154.4^{\circ} + 460^{\circ}) = 614.4^{\circ}\text{R.}$

DENSITY—SPECIFIC GRAVITY

The *density* of a substance is the number of units of mass of the substance contained in one unit of volume. It is usually

expressed in (a) grams per cubic centimeter (g./cc.), (b) grams per liter (g./l.), (c) pounds per cubic foot (lb./cu. ft.).

DENSITY OF GASES

The density of a gas is expressed as (a) the absolute density or simply density and (b) the relative density.

The **density** of a gas is the weight in grams of 1 l. of the gas at standard conditions of temperature and pressure.

The **relative density** of a gas is the weight of a certain volume of the gas compared with the weight of an equal volume of another gas taken as a standard, both gases under the same conditions of temperature and pressure. It is customary to make comparison of the densities of gases at standard conditions, *i.e.*, at 0°C. and 760 mm. of Hg (S.T.P.).

The term **vapor density** is often used synonymously with relative density. In this book it will be used advisedly when hydrogen at 0°C. and 760 mm. of Hg is taken as the basis for comparison. One liter of hydrogen weighs 0.08987 g. at standard conditions. The term relative density will be used where some other gas is used as a basis for comparison.

When determining the density of gases, it becomes necessary to consider that volumes of a definite weight of gas are directly proportional to changes of temperature ($V \propto T$, where V = volume; T = temperature on absolute scale) and inversely proportional to pressure changes ($V \propto 1/P$). Further insight into these conditions leads to the statement that the density of a gas is (a) inversely proportional to changes of temperature and (b) directly proportional to variations of pressure. These facts will be considered in greater detail in Chap. II. Because of the foregoing interdependency in changes of volume and density with variations of temperature and pressure, it is customary, for scientific purposes, to reduce all gas volumes to 0°C. (32°F.), the temperature at which ice melts, and to a pressure of 760 mm. of Hg (1 atm.), or 29.92 in. of Hg. This is termed "standard (or normal) conditions of temperature and pressure." In this text standard conditions is abbreviated as S.T.P. Remember that the pressure of a column of mercury 760 mm. high is, of course, balanced by that of air. This particular pressure of the surrounding air is called "one atmosphere."

One liter of air at 0°C. and 760 mm. (S.T.P.) weighs 1.293 g. The density of air is then 1.293 g./l.

Example.—A volume of carbon dioxide measuring 2,600 cc. at standard conditions was found to weigh 5.148 g. Calculate (a) the density; (b) the vapor density of carbon dioxide.

$$\text{Abs. density} = \text{mass per unit vol.} = \frac{5.148 \text{ g.}}{2.6 \text{ l.}} = 1.98 \text{ g./l. (S.T.P.)}$$

One liter of hydrogen at standard conditions weighs 0.08987 g.

Vapor density =

$$\frac{\text{weight of 1 l. of carbon dioxide at standard conditions}}{\text{weight of 1 l. of hydrogen at standard conditions}}$$

$$\text{Vapor density} = \frac{1.98 \text{ g./l.}}{0.08987 \text{ g./l.}} = 22.03$$

It is pertinent to state briefly that the approximate density of a gas can be obtained from the fact that one gram-molecular weight of any gas occupies 22.4 l. at S.T.P. (molar volume). This very important relationship will be emphasized in greater detail in Chap. V, which deals essentially with molecular weight calculations. The following example will suffice to illustrate the foregoing statement.

Example.—Determine the approximate density of chlorine.

The atomic weight of chlorine = 35.457.

Since chlorine is a diatomic molecule, Cl_2 , the molecular weight of chlorine = $2 \times 35.457 = 70.914$.

From the preceding statement:

22.4 l. of chlorine (S.T.P.) weighs 70.914 g.

1 l. of chlorine (S.T.P.) weighs $\frac{1}{22.4} \times 70.914 \text{ g.} = 3.16 \text{ g.}$

It should be observed that this density of chlorine, 3.16 g./l., is only an approximation and is of value only for approximate calculations. More refined methods give 3.2140 g./l. as the true value for the density of this gas at S.T.P.

SOLIDS AND LIQUIDS

The density of solids and liquids is usually compared with that of water. The relative density compared with water is called the

specific gravity. It is customary to make this comparison with water at 4°C. and atmospheric pressure. This will be done unless otherwise specified. That is,

$$\text{Sp. gr.} = \frac{\text{mass of a certain vol. of the solid or liquid}}{\text{mass of an equal vol. of water at 4°C.}}$$

One cubic centimeter is one one-thousandth of a liter. One cubic centimeter of water at 4°C. weighs 1 g. One cubic centimeter of mercury at 15°C. weighs 13.596 g. The specific gravity of mercury at 15°C. is therefore $\frac{13.596 \text{ g./cc.}}{1.000 \text{ g./cc.}} = 13.596$, or mercury is 13.596 times as heavy as water. If 1 gal. of water weighs 8.34 lb., then a gallon of mercury would weigh $13.596 \times 8.34 = 113.390$ lb.

SOLIDS

As stated before,

Sp. gr. of a solid =

$$\frac{\text{mass of a definite vol. of the solid at given temp.}}{\text{mass of the vol. of water equal to the vol. of the solid}}$$

The mass of the volume of water equal to the volume of the solid is obtained by first weighing the solid in air and then weighing it in water; the difference of these two weighings is the apparent loss in mass of the solid in water. This is the same as the mass of a volume of water equal to the volume of the solid.

W_b = weight of body in air

W_a = weight of body in water

$$\text{Density} = \frac{W_b}{W_b - W_a}$$

The foregoing fully accords with Archimedes' principle which states that a body wholly submerged in a fluid is buoyed up by a force that is equal to the weight of its volume of the fluid. This can be illustrated as follows: Let *A* be a cube 1 cm. on each edge immersed in water and supported by a cord so that it exerts no downward pressure and so that its upper surface is just 1 cm. below the surface of the water. The pressure on a horizon-

tal surface under water is equal to the mass of the column of water having an area equal to that of the surface and a height equal to the distance the surface of the cube is below the surface of the water. The pressure acting downward upon the surface ab is, therefore, 1 g., and the pressure acting upwards on cd is, therefore, 2 g. Consequently, the upward pressure being greater than the downward pressure, there is a buoyant force exerted upon the body, and this force is equal to the difference between the upward and downward forces, or, in this case, 1 g. The volume of water displaced is 1 cc., which, of course, weighs 1 g. Therefore, the body is buoyed up by a force equal to the mass of the volume of water equal to the volume of the body.

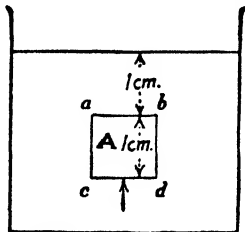


FIG. 3.

Hence the apparent loss in mass of a solid when weighed in air and in water is equal to the mass of its volume of water.

In determining the specific gravity of solids we have the following cases:

(a) When the body is heavier than water, the specific gravity is equal to the mass of the solid in air, divided by its apparent loss of mass when weighed in water. As shown previously, the apparent loss of mass in water is equal to the mass of the volume of water displaced by the solid, this volume of water being, of course, equal to the volume of the solid.

(b) The body is heavier than water but is soluble in it. In order to determine the specific gravity of a substance soluble in water, it is first weighed in air and then in some liquid in which it is insoluble, *e.g.*, in petroleum ether. The specific gravity of the liquid in which it is immersed must, of course, be known. The difference between these two masses is the mass of the volume of petroleum ether which is equal to the volume of the solid.

From this, the specific gravity (compared, of course, to water) can be calculated, as follows:

Example.—A lump of sugar weighs 4.00 g. in air and 2.375 g. when immersed in petroleum ether. The specific gravity of petroleum ether is 0.65. Calculate the specific gravity of sugar.

Mass of sugar in air.....	4.000 g.
Apparent mass of sugar immersed in petroleum ether.....	2.375 g.

1.625 g. = the

mass of the volume of petroleum ether equal to the volume of the lump of sugar.

But we, of course, have in mind that the density of petroleum ether is only 0.65 times that of water. The mass of the volume of water equal to the volume of petroleum ether would be $10/65 \times 1.625 \text{ g.} = 2.5 \text{ g.}$ The specific gravity of the sugar is therefore $4.00 \text{ g.}/2.5 \text{ g.} = 1.60$.

The volume (and consequently the density) of liquids and solid undergoes a change with alteration of temperature. Thus, the density (mass per unit volume) of water at 4°C. is 1.000 g./cc., or 62.43 lb. per cu. ft. At 60°F. (15.5°C.) the density of water is 0.99905 g./cc., or 62.37 lb. per cu. ft. With solids the volume changes due to changing temperature conditions are generally insignificant.

Variation of pressure has very little effect on the volume of solids or liquids; hence, except in problems of the most refined accuracy, the pressure need not be stated in giving the density of solids or liquids.

(c) A powder insoluble in water.

Weigh a small flask or pycnometer (a convenient kind is shown in Fig. 4). Suppose that the mass is 8.754 g.



FIG. 4.

Fill the flask and capillary with water, and weigh again. Assume this mass to be 20.004 g. The difference in the mass is, of course, the mass of water that just fills the flask. This difference is 11.250 g.

Mass of the powder in air, 3.556 g.

Remove the stopper. Introduce the powder into the flask. Replace the stopper. The powder introduced will displace its volume of water, and this will overflow through the capillary when the stopper is replaced. Now weigh again. Mass of flask, powder, and enough water to fill, 21.782 g.

Let *A* equal weight of flask filled with water plus weight of powder in air, and *B* equal weight of flask with powder and enough water to fill it. The difference, *A* minus *B*, equals the mass of water displaced.

The flask filled with water	= 20.004 g.
The mass of the powder in air	= <u>3.556 g.</u>
A	= 23.560 g.
B	= <u>21.782 g.</u>
A - B = the mass of water displaced	= 1.778 g.
Since the mass of powder in air	= 3.556 g.
And the mass of its volume of water	= 1.778 g.
Then, the sp. gr. of the powder	= $\frac{3.556 \text{ g.}}{1.778 \text{ g.}} =$
2.00	

LIQUIDS

The specific gravity of liquids may be determined by means of a (a) pycnometer, (b) hydrometer, or (c) Westphal balance.

In using the pycnometer, M , the mass of the liquid that just fills the pycnometer, is determined; L , that mass of pure water at 4°C. which just fills the pycnometer at the same temperature, is determined. The ratio $M:L$ is, of course, the specific gravity of the liquid at that temperature.

The common hydrometer consists of a thin glass tube having at its lower end a weighted bulb which floats in the liquid. The depth to which the bulb sinks is determined by the density of the liquid and is observed on a scale engraved upon the stem of the hydrometer. The specific gravity of the liquid in which it is floating may be read by observing the mark that is just at the surface. It is to be noted that the scale is not of equal divisions.

The Baumé Scale.—This is a type of specific gravity hydrometer, designed by the French chemist Antoine Baumé, which has equal scale divisions and is purely arbitrary. It is in common use in the heavy chemicals industry for density determinations of liquids. The scale readings do not give directly the specific gravity of liquids. There are two Baumé scales, one applying to liquids heavier than water, and the other to liquids lighter than water. The relationship between the specific gravity and degrees Baumé is given as follows:

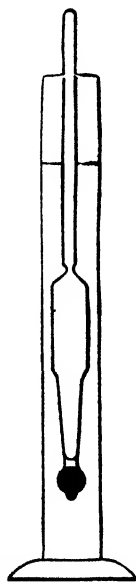


FIG. 5.

(a) For liquids heavier than water (60°F.),

$$\text{Degrees Baumé (°Bé.)} = 145 - \frac{145}{\text{sp. gr.}}$$

or

$$\text{Sp. gr.} = \frac{145}{145 - \text{°Bé.}}$$

(b) For liquids lighter than water (60°F.),

$$\text{°Bé.} = \frac{140}{\text{sp. gr.}} - 130$$

or

$$\text{Sp. gr.} = \frac{140}{130 + \text{°Bé.}}$$

The graduations on the Baumé scale were originated as follows: For liquids heavier than water, the hydrometer is immersed in a 15 per cent NaCl solution (12.5°C.), and the point to which it sinks is marked 15°. The point to which the instrument sinks in pure water is marked 0°. The space between these two marks is then divided into 15 equal spaces, and the graduation is continued down the stem. For liquids lighter than water, the hydrometer is placed in a 10 per cent salt solution; the point to which it sinks is marked 0°; and the point to which it sinks in pure water is marked 10°. The space between these two marks is divided into 10 equal spaces, and these graduations are extended up the stem of the hydrometer.

The A.P.I. Scale.—A special specific gravity scale which has been adopted by the American Petroleum Institute (A.P.I.) for expressing the densities of petroleum products is known as the A.P.I. scale. The relation between degrees A.P.I. and specific gravity is similar to the Baumé scale for liquids lighter than water and is given as follows:

$$\text{Degrees A.P.I.} = \frac{141.5}{\text{sp. gr.}} - 131.5(60^\circ\text{F.})$$

The Significance of Specific Gravity of Aqueous Solutions.—In dealing with aqueous solutions of acids, bases, and salts it is

customary to state the specific gravity of the solution and the percentage by weight of the solute in a definite volume of the solvent (concentration). For example, "oil of vitriol" is a sulfuric acid solution which has a specific gravity of 1.83 and contains approximately 93 per cent by weight of active H_2SO_4 . The specific gravity tells us that 1 cc. of sulfuric acid weighs 1.83 times as much as 1 cc. of water at the same temperature. Since 1 cc. of water weighs 1 g. at 4°C ., then 1 cc. of this sulfuric acid solution will weigh 1.83 g. The acid solution is not pure; *i.e.*, it contains 93 per cent by weight of active H_2SO_4 (there is 7 per cent by weight of H_2O mixed with the acid). Then every 100 g. of this solution contains 93 g. of active H_2SO_4 , and 1 g. of the acid will contain 0.93 g. of active H_2SO_4 . The actual weight of active H_2SO_4 in 1 cc. of this sulfuric acid solution ("oil of vitriol") would then be 0.93×1.83 , or 1.7019 g.

Example.—How many cubic centimeters of nitric acid solution, specific gravity 1.4010 and containing 65.67 per cent by weight of HNO_3 , will contain 63.0 g. of active HNO_3 ?

The specific gravity of the acid solution is 1.4010, or 1 cc. of this acid weighs 1.4010 g. Since the acid contains 65.67 per cent by weight of HNO_3 , then $1.4010 \times 0.6567 = 0.920$ g. of active HNO_3 in 1 cc. of nitric acid solution.

One gram of active HNO_3 is contained in $1/0.92$, or 1.087 cc., of nitric acid solution.

Sixty-three grams of active HNO_3 will be contained in $63 \times 1.087 = 68.48$ cc. of this nitric acid solution.

Problems

1. Fill in the blank spaces in the table to show the equivalence of grams and milligrams:

Weight in grams (g.)	Weight in milligrams (mg.)
2.5768 g.	mg.
0.0356 g.	mg.
0.0008 g.	mg.
0.5432 g.	mg.
0.0077 g.	mg.

2. Show the equivalence of milligrams and grams in the following table:

Weight in milligrams (mg.)	Weight in grams (g.)
0.20 mg.....	g.
32.50 mg.....	g.
3,143.6 mg.....	g.
2.7 mg.....	g.
255.2 mg.....	g.

3. Convert the following weights in grams to their equivalence in milligrams:

Weight in grams (g.)	Weight in milligrams (mg.)
0.0005 g.....	mg.
0.0555 g.....	mg.
5.5005 g.....	mg.
0.0055 g.....	mg.
0.5505 g.....	mg.

4. Make the conversions of each of the values as indicated in the following table:

0.5 m.....	mm.
50.0 cm.....	m.
0.05 kg.....	g.
500.0 ml.....	l.
250.0 mg.....	g.

5. Supply the conversions in the following table for each of the values as shown:

10^{-3} cm.....	μ
743.7 A.....	cm.
0.25 mg.....	g.
250.0 ml.....	l.
50.0 kg.....	g.

6. The wave length of the red cadmium spectral line, the primary standard of wave length measurements, is 0.000064384696 cm. Express this wave length in (a) microns; (b) millimicrons; (c) angstrom units.
7. The characteristic wave lengths of the K series of X radiation produced by X-ray tubes equipped with various metallic targets are listed in angstrom units in the following table:

Molybdenum,	$K\alpha_1 = 0.70783 \text{ \AA}$.
Tungsten,	$K\alpha_1 = 0.20862$
Calcium,	$K\alpha_1 = 3.35332$
Copper,	$K\alpha_1 = 1.537395$
Chromium,	$K\alpha_1 = 2.28503$

Express these wave lengths in terms of (a) centimeters; (b) microns; (c) X units.

8. An X-ray tube equipped with a tungsten target operating at varying voltages produces minimum short wave lengths as follows:

100,000 volts.....	0.12345 \AA.
220,000 volts.....	0.05611 \AA.
400,000 volts.....	0.03086 \AA.
500,000 volts.....	0.02469 \AA.
1,000,000 volts.....	0.01234 \AA.

Express these wave lengths in terms of (a) centimeters; (b) microns; (c) X units.

9. An ultraviolet lamp emits 95 per cent of its radiation at a wave length of 2537 \AA. Express this wave length in terms of (a) centimeters; (b) millimicrons; (c) microns.
10. The shortest visible waves and the longest visible waves of the electromagnetic spectrum are 0.000037 and 0.000067 cm. in length, respectively. Express these wave lengths in (a) microns; (b) millimicrons; (c) angstrom units.
11. Make the temperature conversions as indicated in the following table:

$^{\circ}\text{A.}$	$^{\circ}\text{C.}$	$^{\circ}\text{F.}$	$^{\circ}\text{R.}$
212 $^{\circ}$	-32 $^{\circ}$	0 $^{\circ}$	
		-148 $^{\circ}$	672 $^{\circ}$

12. Fill in the spaces in the following table with the corresponding temperature conversions:

°A.	°C.	Reading	°F.	°R.
—	—	-100°C. - 40°F. 100°A. 500°R. 600°F.	—	—

13. Construct a temperature conversion table from the following data: The middle column of numbers refers to temperature readings in either degree centigrade or degree Fahrenheit, which it is desired to convert into readings on the other scale. Thus, if converting a reading in degree Fahrenheit to degree centigrade, the equivalent temperature is to be placed opposite this number in the left-hand column, and when a reading in degree centigrade is to be converted to degree Fahrenheit, the equivalent temperature is to be placed opposite this number in the right-hand column:

(a)

°C.	Reading	°F.
	0	
	1	
	2	
	3	
	4	
	20	
	21	
	22	
	23	
	24	

(b)

°C.	Reading	°F.
	100	
	105	
	110	
	115	
	125	
	500	
	510	
	520	
	530	
	540	

Hint: $1^{\circ}\text{C.} = \frac{9}{5}^{\circ}\text{F.}$, and $1^{\circ}\text{F.} = \frac{5}{9}^{\circ}\text{C.}$

14. What is meant by the term "absolute zero"? How is the absolute Kelvin scale constructed? What is the difference in expressing temperatures on the absolute Kelvin scale and on the absolute Rankine scale?
15. Convert the following temperatures to their corresponding values on the centigrade scale: 2°F. , 2000°F. , 200°F. , -20°F. , -200°F.
Ans. -16.67°C. ; 1093.33°C. ; 93.33°C. ; -28.88°C. ; -128.8°C.
16. Convert 16°C. , 160°C. , -16°C. , 1600°C. , 600°C. to the corresponding values on the Fahrenheit scale.
Ans. 60.8°F. ; 320°F. ; 3.2°F. ; 2912°F. ; 1112°F.

17. What temperatures on the absolute Kelvin scale correspond to -180°C ., 0°F ., -40°F ., 100°C ., 200°F .?

Ans. 93°A .; 255.23°A .; 233°A .; 373°A .; 366.33°A .

18. Calculate the temperature on the Fahrenheit scale that has a reading exactly five times the reading on the centigrade scale. *Ans.* $+50^{\circ}\text{F}$.

19. What points on the Fahrenheit and centigrade scales correspond to 225°A .? *Ans.* -54.4°F .; -48°C .

20. Ethyl alcohol freezes at -117.6°C . and boils at 78.4°C . Determine the corresponding temperatures on (a) the Fahrenheit scale, (b) the absolute Rankine scale. *Ans.* (a) -179.68°F .; 173.12°F .

21. During an experiment, a Fahrenheit thermometer showed a temperature change of 30° . Calculate the value of this temperature change in centigrade degrees. *Ans.* 16.66°C .

22. (a) Liquid oxygen boils at -297.4°F .
 (b) Liquid ammonia boils at -37.3°F .
 (c) Liquid hydrogen boils at -423°F .
 (d) Liquid nitrogen boils at -321°F .

Calculate the corresponding values on (a) the centigrade scale; (b) the absolute Rankine scale.

Ans. (a) -183.0°C .; (b) -255.37°C .; (c) -252.77°C .; (d) -196.11°C .

23. The melting points of five common metals expressed in degrees centigrade are as follows:

- (a) Platinum, 1755°C .
 (b) Aluminum, 658.7°C .
 (c) Copper, 1083°C .
 (d) Gold, 1063°C .
 (e) Silver, 960.5°C .

Calculate the corresponding temperatures on the Fahrenheit scale.

Ans. (a) 3191°F .; (b) 1217.66°F .; (c) 1981.4°F .; (d) 1945.4°F .;
 (e) 1760.9°F .

24. The melting points of five common metals expressed in degrees Fahrenheit are:

- (a) Antimony, 1166°F .
 (b) Bismuth, 520°F .
 (c) Cadmium, 609.5°F .
 (d) Tin, 449.4°F .
 (e) Zinc, 786.9°F .

Determine the corresponding values on the centigrade scale.

Ans. (a) 630.0°C .; (b) 271.11°C .; (c) 320.83°C .; (d) 231.88°C .;
 (e) 419.39°C .

25. Calculate the vapor density of nitrogen, given that 5 l. of this gas, at standard conditions, weighs 6.2535 g. *Ans.* 13.91.

26. At standard conditions, 50 cc. of chlorine weighs 0.161 g. Calculate the vapor density of chlorine. *Ans.* 35.81.

27. Calculate the vapor density of oxygen, 3 l. of which, at standard conditions, weighs 4.2873 g. *Ans.* 15.89.
28. A piece of granite weighs 2.36 g. in air and 1.56 g. in water at 4°C. Calculate the specific gravity of this specimen of granite. *Ans.* 2.95.
29. Starting with the premise that 1 cc. of water at 4°C. weighs 1 g., calculate (a) the weight of 1 gal. of water at 4°C. in pounds; (b) the weight of 1 cu. ft. of water at 4°C. in pounds. *Ans.* (a) 8.34 lb.
30. Determine the specific gravity of a sample of red slate from the following data:
- | | |
|----------------------------------------------------------|------------|
| Weight of sample in air..... | 5.0 g. |
| Weight of pycnometer empty..... | 18.4786 g. |
| Weight of pycnometer filled with water..... | 37.9708 g. |
| Weight of pycnometer + sample + enough water to fill it. | 41.0307 g. |
- Ans.* 2.58.
31. Determine the specific gravity of a sample of a powdered mineral from the following data:
- | | |
|----------------------------------------------------------|------------|
| Weight of sample in air..... | 3.0 g. |
| Weight of pycnometer empty..... | 13.2014 g. |
| Weight of pycnometer filled with water..... | 37.8103 g. |
| Weight of pycnometer + sample + enough water to fill it. | 39.6307 g. |
- Ans.* 2.54.
32. A bottle holds 336 g. of water when just full; it holds 570 g. of sulfuric acid. Calculate the specific gravity of the acid. *Ans.* 1.695.
33. Calculate the specific gravity of an oil from these data:
- | | |
|---------------------------------------------|------------|
| Weight of pycnometer..... | 18.1482 g. |
| Weight of pycnometer filled with water..... | 64.4932 g. |
| Weight of pycnometer filled with oil..... | 48.9615 g. |
- Ans.* 0.664.
34. Calculate the specific gravity of a sample of ground ore from the following data:
- | | |
|-------------------------------------------------------------|---------|
| Weight of sample in air..... | 3.0 g. |
| Weight of pycnometer filled with water..... | 26.5 g. |
| Weight of pycnometer, sample, and enough water to fill..... | 28.5 g. |
- Ans.* 3.0.
35. A bottle weighs 50.5 g. The bottle filled with water weighs 258.58 g. The bottle filled with oil weighs 220.2 g. Calculate (a) the capacity of the bottle, (b) the specific gravity of the oil. *Ans.* (a) 208.08 cc.; (b) 0.815.
36. A piece of glass weighs 258.6 g. in air, 152.6 g. in water at 4°C. and 92 g. in sulfuric acid. Calculate the specific gravity of the sulfuric acid. *Ans.* 1.571.

37. Calculate the weight of 1 gal. of turpentine the specific gravity of which is 0.873. One gallon of water weighs 8.345 lb. *Ans.* 7.285 lb.
38. Calculate the volume of 50 lb. of linseed oil of specific gravity 0.926. One gallon of water weighs 8.345 lb. *Ans.* 6.469 gal.
39. Given a solution of nitric acid, specific gravity 1.25, containing 39.82 per cent of HNO_3 by weight. Calculate the weight of HNO_3 in 10 cc. of the solution. *Ans.* 4.9775 g.
40. A hydrochloric acid solution has a specific gravity of 1.19 and contains 39.8 per cent by weight of HCl . Calculate the number of cubic centimeters of this acid solution that will contain 25.0 g. of HCl . *Ans.* 52.78 cc.
41. How many cubic centimeters of sulfuric acid, specific gravity 1.526, containing 62 per cent by weight of H_2SO_4 , will contain 100 g. of H_2SO_4 ? *Ans.* 105.6 cc.
42. A railroad tank car is capable of holding 80,000 lb. of sulfuric acid. (a) How many gallons of sulfuric acid, 66° Bé. at 60°F., would be contained in the car? (b) If this acid contains 93.19 per cent by weight of H_2SO_4 , how many pounds of active H_2SO_4 is available in the tank car? *Ans.* (a) 5,291.7 gal.; (b) 74,552 lb.
43. Technically pure mercury is obtained in iron flasks holding 76 lb. of mercury at a cost of \$212.80 (Nov. 4, 1939). (a) How many (i) cubic centimeters, (ii) quarts, of mercury are contained in the flask? (b) What is the cost of (i) 100 cc. and (ii) 1 qt. of mercury? The density of Hg is 13.596. *Ans.* (ai) 2,535 cc.; (aii) 2.68 qt.
44. Determine the weight of NaOH in 5 l. of sodium hydroxide solution which has a specific gravity of 1.153 and contains 14 per cent by weight of NaOH . (b) Calculate the number of cubic centimeters of this caustic soda solution that will contain 20 g. of NaOH . *Ans.* (a) 807.1 g.; (b) 123.9 cc.
45. (a) What weight of Na_2CO_3 is contained in 250 cc. of sodium carbonate solution having a specific gravity of 1.1029 and containing 10 per cent by weight of Na_2CO_3 ? (b) How many cubic centimeters of this solution will contain 10 g. of Na_2CO_3 ? *Ans.* (a) 27.57 g.; (b) 90.6 cc.
46. (a) Calculate the weight of 10 gal. of sulfuric acid having a specific gravity of 1.615 and containing 70 per cent by weight of H_2SO_4 . (b) How many gallons of this acid solution will contain 184 lb. of active H_2SO_4 ? *Ans.* (a) 134.0 lb.; (b) 19.6 gal.
47. A carboy holds 100 lb. of water or 183.9 lb. of sulfuric acid. (a) What is the capacity of the carboy in gallons? (b) Calculate the specific gravity of the acid at 4°C. *Ans.* (a) 12.0 gal.; (b) 1.839.
48. Pure iron has a specific gravity of 7.85. (a) What is the density in pounds per cubic inch? (b) Calculate the weight of an iron bar 25 ft. long and $1\frac{1}{2}$ in. square. *Ans.* (a) 0.282 lb. per cu. in.; (b) 190.35 lb.
49. The specific gravity of platinum is 21.37. A piece of platinum wire has a diameter of 0.92 mm. What length of this wire will weigh 1.1 g.? *Ans.* 77.32 mm.

50. Twelve inches of hard-drawn copper wire weighs 0.0078 lb. The specific gravity of the copper is 8.9. Calculate the diameter of the wire.
Ans. 0.0507 in.
51. Cast gold has a specific gravity of 19.3. Calculate the weight of a piece of gold that displaces 9.5 cc. of water.
Ans. 183.35 g.
52. A 100-cc. graduated cylinder contains water up to the 75-cc. mark; 25 g. of rhombic sulfur is put into this graduate. The specific gravity of rhombic sulfur is 2.04. What will be the final reading of the water level in the cylinder?
Ans. 87.2 cc.

Additional Problems without Answers, for Quizzes

53. What points on the centigrade and Fahrenheit scales correspond to 200°A.? 200°R.?
54. Calculate the temperature at which the readings on the Fahrenheit and centigrade scales are the same.
55. The melting points of five metals expressed in degrees centigrade are as follows:

Beryllium, 1280°C.
Chromium, 1615°C.
Cobalt, 1480°C.
Tungsten, 3400°C.
Magnesium, 651°C.

Express the foregoing temperatures in degrees Fahrenheit.

56. The melting points of five alloys expressed in degrees Fahrenheit are as follows:

Magnalium (90 Al, 10 Mg), 1126.4°F.
Woods metal (50 Bi, 25 Pb, 12.5 Sn, 12.5 Cd), 149.9°F.
Invar (63.8 Fe, 36 Ni, 0.2 C), 2726.6°F.
Monel metal (60 Ni, 33 Cu, 6.5 Fe), 2480°F.
Antifriction (75 Sn, 12.5 Sb, 12.5 Cu), 451.4°F.

Express the foregoing temperatures in degrees centigrade.

57. The melting points of five alloys expressed in degrees centigrade are as follows:

Bell metal (78 Cu, 22 Sn), 870°C.
Red brass (85 Cu, 15 Zn), 1030°C.
Platinite (53.85 Fe, 46 Ni, 0.15 C), 1470°C.
Nichrome (60 Ni, 24 Fe, 16 Cr), 1350°C.
Nickel steel (96.5 Fe, 3.5 Ni), 1530°C.

Express the foregoing temperatures in degrees Fahrenheit.

58. The melting points of five refractory materials in degrees Fahrenheit are as follows:

Silica, SiO_2 , 3182°F.
Magnesia, MgO , 5072°F.

Zirconia, ZrO_2 , 4892°F .
 Chromite brick, 3956°F .
 Bauxite brick, 3308°F .

Express the foregoing temperatures in degrees centigrade.

59. The critical temperatures and critical pressures of the noble gases are as follows:

Helium, He, 5°A . at 2.75 atm.
 Neon, Ne, 53°A . at 29 atm.
 Argon, A, 156°A . at 52 atm.
 Krypton, Kr, 210°A . at 54.3 atm.
 Xenon, Xe, 258°A . at 54 atm.

Express the foregoing temperatures in degrees centigrade and Fahrenheit.

60. Supply the corresponding temperatures of the different scales in the blank spaces:

Substances	$^\circ\text{C}$.	$^\circ\text{F}$.	$^\circ\text{A}$.
Mercury boils at.....	356.9		
The critical temperature of carbon monoxide is.....			131.9
The boiling point of argon is.....	-186.0		
The freezing point of neon is.....			20.0

61. The critical temperatures and critical pressures of some gases commonly used as refrigerants are as follows:

Gases	$^\circ\text{C}$.	$^\circ\text{F}$.	$^\circ\text{A}$.	Critical pressures, atm.
Ammonia.....		266.00	..	115.0
Carbon dioxide.....	31.1	73.0
Sulfur dioxide.....		311.72	..	78.9
Air, liquid.....	-140.0	39.0

Supply the corresponding temperatures of the different scales in the blank spaces.

62. Under standard conditions 500 cc. of a gas weighs 0.982 g. Calculate the relative density of the gas compared with (a) air, (b) chlorine.
 63. The relative density of a gas with respect to air is 2.265. Calculate the weight of 1 l. of the gas, at standard conditions.
 64. The density of each of the noble gases in grams per liter at S.T.P. is as follows:

Helium, 0.1782

Neon, 0.9002

Argon, 1.7809

Krypton, 3.7080

Xenon, 5.8510

Determine (a) the vapor density of each gas; (b) the relative density of each gas compared with air as the standard.

65. The density of each of five gases commonly used in the chemical laboratory in grams per liter at S.T.P. is as follows:

Hydrogen sulfide, 1.5392

Chlorine, 3.2140

Ammonia, 0.7708

Carbon dioxide, 1.9768

Nitrogen, 1.2507

Calculate (a) the vapor density of each gas; (b) the relative density compared with air as a standard.

66. The vapor density of each of four gaseous fuels is as follows:

Acetylene, C_2H_2 , 13.120Ethane, C_2H_6 , 15.090Ethylene, C_2H_4 , 14.030Methane, CH_4 , 7.976

Calculate (a) the density of each of these gases in grams per liter at S.T.P.; (b) the relative density of each gas referred to air as the standard.

67. A volume of 200 cc. of a liquid weighs 250 g. What is the specific gravity of the liquid?
68. Calculate the volume of 150 lb. of cottonseed oil, the specific gravity of which is 0.926.
69. Calculate the specific gravity of glycerin 15 cc. of which weighs 18.9 g.
70. Calculate the specific gravity of a liquid from the following:

Weight of pycnometer, empty.....	18.1472 g.
Weight of pycnometer filled with water.....	64.4635 g.
Weight of pycnometer filled with liquid.....	48.9600 g.

71. Determine the specific gravity of linseed oil from the following data:

Pycnometer + water at 15.5°C.....	53.1840 g.
Pycnometer + linseed oil at 15.5°C.....	51.4536 g.
Pycnometer.....	27.0121 g.

72. Calculate the specific gravity of a drying oil from the following data:

Weight of pycnometer + H_2O at 15.5°C.....	60.9114 g.
Weight of pycnometer + oil at 15.5°C.....	59.3296 g.
Weight of pycnometer.....	33.0612 g.

73. A glass ball weighs 9.25 g. in air, 8.2 g. in water, and 8.36 g. in gasoline. What is the specific gravity of the gasoline?
74. A pycnometer weighs 16.525 g., 35.639 g. when filled with water, and 42.778 g. filled with a liquid. Calculate the specific gravity of the liquid.
75. A sample of KOH weighs 11.3 g. in air and 7.4 g. when immersed in oil. The specific gravity of the KOH is 2.00. Calculate the specific gravity of the oil.
76. A body weighs 9.2 g. in air, 7.5 g. in water, and 8.5 g. in oil. Calculate the specific gravity of the oil.
77. A piece of iron pyrites weighs 4.894 g. in air and 3.89 g. in water. Calculate the specific gravity of the pyrites.
78. Calculate the specific gravity of a piece of metal that weighs 15 g. and displaces 10 cc. of water.
79. The specific gravity of iron is 7.28. Calculate the weight in grams of a piece of iron that has a volume of 230 cc.
80. A piece of metal weighs 2.9476 g. in air and 2.6470 g. when immersed in water. Calculate (a) the specific gravity of the metal; (b) the weight of a cube of the metal which measures 3 cm. on an edge; (c) the volume of 2 kg. of the metal.
81. Calculate the specific gravity of a metal from the following:
- | | |
|--------------------------------------------------------------------|-----------|
| Weight of sample in air..... | 2.500 g. |
| Weight of pycnometer, empty..... | 4.420 g. |
| Weight of pycnometer, filled with water..... | 10.455 g. |
| Weight of pycnometer, containing sample and filled with water..... | 12.665 g. |
82. Calculate the specific gravity of sand from the following data:
- | | |
|---------------------------------------------------------|------------|
| Weight of bottle..... | 26.8990 g. |
| Weight of sand..... | 3.1255 g. |
| Weight of sand and bottle and enough water to fill..... | 66.7250 g. |
| Weight of bottle filled with water..... | 64.7990 g. |
83. A steel casting of a machine part weighs 1,250 lb. Determine the weight of this machine part if the alloy magnalium was used in making the casting. The specific gravity of steel is 7.83. The specific gravity of magnalium is 2.5.
84. The specific gravity of sulfuric acid is 1.83. This acid contains 92.10 per cent by weight of H_2SO_4 . Calculate the number of grams of H_2SO_4 contained in 25 cc. of this sulfuric acid.
85. The specific gravity of a shipment of nitric acid is 1.420. This acid contains 69.8 per cent by weight of HNO_3 . Calculate the number of cubic centimeters of this nitric acid that will contain 10 g. of HNO_3 .
86. The specific gravity of a potassium hydroxide solution is 1.424. This solution contains 40.9 per cent of KOH by weight. Calculate the number of grams of KOH that is contained in 50 cc. of this solution.
87. How many cubic centimeters of sodium hydroxide solution will contain 20 g. of NaOH if the solution of sodium hydroxide in question has a specific gravity of 1.383 and contains 35 per cent by weight of NaOH?

88. A steel drum holds 250 l. of ethyl alcohol (sp. gr. of 0.8161 and containing 90 per cent by weight of C_2H_5OH). Calculate (a) the weight of alcohol in the drum; (b) the number of cubic centimeters of this solution that contains 100 g. of C_2H_5OH .
89. Sulfuric acid made by the lead-chamber process has a density of 51.7° Bé. at 60°F. Express the weight of this acid in (a) grams per liter; (b) pounds per gallon; (c) pounds per cubic foot.
90. (a) The density of sulfuric acid as obtained from the contact process is 66° Bé. at 60°F. Determine the weight in pounds of a carboy (capacity 12 gal.) of this concentrated sulfuric acid. (b) What is the weight of this acid in pounds per cubic foot?
91. Glacial acetic acid has a specific gravity of 1.0524 and contains 99 per cent by weight of $HC_2H_3O_2$. (a) What weight of $HC_2H_3O_2$ is contained in 2.5 l. of this acid solution? (b) How many cubic centimeters of this solution will contain 25 g. of $HC_2H_3O_2$?
92. An acid solution is made by diluting 25 cc. of sulfuric acid (sp. gr. 1.8354 and containing 93.19 per cent H_2SO_4) with sufficient water to make 1 l. of solution. Calculate the weight of H_2SO_4 in 25 cc. of this solution.
93. A dilute nitric acid solution is made by diluting 6.4 cc. of nitric acid (sp. gr. 1.4134 and containing 70 per cent by weight of HNO_3) to 1 l. Calculate the weight of HNO_3 in 100 cc. of this solution.
94. A dilute basic solution is obtained by diluting 80 cc. of caustic soda solution (sp. gr. 1.39 and containing 36 per cent by weight of $NaOH$) to 1 l. How many cubic centimeters of this solution contains 1 g. of $NaOH$?
95. A dilute basic solution is made by diluting 100 cc. of caustic potash solution (sp. gr. 1.399 and containing 40 per cent by weight of KOH) to 1 l. Calculate the number of cubic centimeters of this solution that will contain 10 g. of KOH .
96. A dilute acid solution is made by diluting 100 cc. of hydrochloric acid (sp. gr. 1.2003 and containing 39.86 per cent by weight of HCl) to 1 l. How many cubic centimeters of this solution will contain 5 g. of HCl ?

CHAPTER II

OUTLINE

Kinetic explanation of the behavior of a gas.

Boyle's Law. Volume of a gas is inversely proportional to the pressure if temperature is kept constant.

Standard pressure.

Gay-Lussac's Law. The volume of a gas is directly proportional to the absolute temperature if pressure is kept constant.

The density of a gas is directly proportional to the pressure if the temperature is kept constant.

Increase in temperature decreases the density if pressure is constant.

Effect of temperature and pressure together on the density of a gas.

Partial pressure—Dalton's Law. The total pressure of a mixture of gases may be regarded as the sum of the pressures that each gas would exert if it alone occupied the entire space.

Vapor pressure of water.

EFFECT OF CHANGES IN PRESSURE AND TEMPERATURE ON THE VOLUME OF GASES

Very careful measurements have indicated that the molecules of which substances are composed are very nearly incompressible; *i.e.*, when subjected to tremendous pressure each molecule contracts only a very small amount in size. Solids and liquids decrease only slightly in volume when subjected to tremendous pressure. This indicates that in solids and liquids the molecules are packed closely together. In the case of gases we naturally assume that the molecules are separated from one another. This assumption is confirmed by the fact that the volume of a gas is decreased by increasing the pressure on the gas. We know that the molecules of gases are moving—that they are traveling in sensibly straight lines at high speeds, colliding, rebounding, and continuing their travel in other directions. It is assumed that they are perfectly elastic, in accord with the fact that no energy is lost by the collisions. A great many of the molecules are, of course, continually colliding with the walls of the vessel. These repeated collisions exert a pressure on the walls and balance the pressure acting on the gas. Thus, consider a gas contained in a cylinder subject to a pressure P as shown in Fig. 6.

The pressure caused by the collision of the particles against the walls balances the pressure P and prevents the piston from moving down. The speed of a molecule is dependent on the temperature. The higher the temperature the greater the speed of the molecule, and consequently the greater the energy that it possesses. If a gas is heated, the speed of the molecules is increased; the energy increased; the number of collisions per minute increased; and the pressure on the walls, due to collisions with the walls, increased. If the temperature is decreased, the speed of the molecules is decreased, their energy decreased, the number of collisions per minute on the walls decreased, and the pressure on the walls decreased.

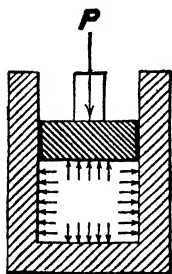


FIG. 6.

If the temperature of the gas is kept constant, and the pressure increased, the molecules will be crowded together; *i.e.*, the volume of the gas will be decreased. Because of this crowding, the collisions will become more frequent as the molecules are brought closer together, and the increased number of collisions will cause increased pressure on the walls sufficient to balance the increased external pressure.

The exact numerical effect of increase of pressure upon the volume of gases was first found by Boyle in 1660. Boyle com-

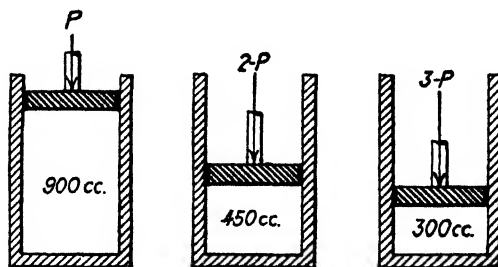


FIG. 7.

pressed air in the short closed leg of a U tube, using varying amounts of mercury as a compressing agent. He concluded from his experiments that, temperature remaining constant, **the volume of a gas is inversely proportional to the pressure.** This

relation is known as Boyle's Law of Gases. It may be illustrated as follows:

Consider a cylinder (Fig. 7) containing 900 cc. of a gas, under a pressure P . If the pressure is doubled, the gas will be compressed until it occupies one-half its original volume; *i.e.*, its volume under a pressure $2P$ will be 450 cc. If the pressure is increased to $3P$, the volume will be reduced to 300 cc.; and so on.

STANDARD PRESSURE

It is a familiar fact that the pressure of the atmosphere fluctuates from day to day. The instrument used for measuring atmospheric pressures is known as a **barometer** and originated in 1644 with E. Torricelli. In its simplest form a barometer consists of a straight glass tube about 8.5 mm. in diameter and 80 to 85 cm. in length, closed at one end. It is completely filled with purified mercury which is boiled in the tube in order to eliminate any entrapped air or moisture, then with a stopper held against its open end is placed under the surface of the mercury in a shallow open vessel, and the tube inverted. It will be noticed that the mercury falls in the tube to a height of approximately 76 cm. (29.92 in.) above the level of the mercury in the dish. The space in the tube above the mercury is familiarly known as "Torricelli's vacuum." It is of interest to note that Torricelli concluded that the column of mercury was maintained at this height (76 cm.) by the atmosphere pressing down on the surface of the mercury in the open vessel.

Since the pressure of the atmosphere varies greatly with altitude and with varying weather conditions, it follows naturally that volumes (and densities) of gases are subjected to changes. As a basis for comparison of volumes (and densities) of gases, it is customary to refer to the **normal, or standard, pressure**. This is equal to the weight of a column of mercury of unit cross-sectional area and 760 mm. high at sea level, is approximately the average pressure of the atmosphere at sea level, and is frequently called one atmosphere (atm.). The density of mercury is 13.596. Thus a column of mercury 76 cm., or 29.92 in., in height is equivalent to a column of water 33.91 ft. high. Also, a column of mercury 76 cm. in height corresponds to a weight of

$76 \times 13.596 = 1,033.3$ g. per unit cross-sectional area (per square centimeter), or 14.7 lb. per sq. in. at sea level.

TABLE VII.—CONVERSION TABLE FOR PRESSURE

Lb. per sq. in.	Lb. per sq. ft.	Inches of mercury	Mm. of mercury	Cm. of mercury	Feet of water	Inches of water
14.7	2116.8	29.92	760	76.0	33.91	406.9
1	144	2.036	51.706	5.1706	2.307	27.68
0.4913	70.75	1	25.40	2.54	1.1322	13.59
0.433	62.40	0.8819	22.4	2.24	1.0	12.00

EFFECT OF TEMPERATURE

It has been found by experiment that a gas if kept at constant pressure will expand $\frac{1}{273}$ of the volume that it occupies at 0°C . (273°A .) for each 1°C . that it is heated. Similarly, it will contract $\frac{1}{273}$ of its volume at 0°C . for each 1°C . that it is cooled (pressure kept constant). Thus:

becomes	273 cc. of any gas at	0°C . (273°A .)
	274 cc. at	1°C . (274°A .)
	275 cc. at	2°C . (275°A .)
	373 cc. at	100°C . (373°A .)
	272 cc. at	-1°C . (272°A .)
	271 cc. at	-2°C . (271°A .)
	173 cc. at	-100°C . (173°A .)
	73 cc. at	-200°C . (73°A .)
	23 cc. at	-250°C . (23°A .)
	Etc.	

This relation between increase in volume and increase in temperature was first stated in the form of a law by Gay-Lussac in 1801: **Pressure remaining constant, the volume of a gas is directly proportional to the absolute temperature.**

Example 1.—What volume will 10 l. of a gas, measured at 0°C ., occupy at 100°C ., pressure remaining constant?

$$0^{\circ}\text{C}. = 273^{\circ}\text{A}. \quad 100^{\circ}\text{C}. = 373^{\circ}\text{A}.$$

The temperature is increased from 273°A . to 373°A ., and the volume will accordingly be increased (Gay-Lussac's Law). Consequently, *the original volume must be multiplied by a fraction*

greater than one, or $10 \text{ l.} \times \frac{373}{273} = 13.66 \text{ l.} = \text{the new volume.}$

Example 2.—A gas occupies 3 l., measured at 32°C. and atmospheric pressure. What volume will it occupy if the temperature is changed to 18°C. , the pressure remaining unchanged?

$$32^{\circ}\text{C.} = 305^{\circ}\text{A.} \quad 18^{\circ}\text{C.} = 291^{\circ}\text{A.}$$

It is first noted that the gas is cooled from 305°A. to 291°A. , and the volume will consequently be decreased (Gay-Lussac's Law). Thus, *the original volume must be multiplied by a fraction smaller than one*, or $3 \text{ l.} \times \frac{291}{305} = 2.86 \text{ l.} = \text{the new volume.}$

EFFECT OF CHANGES OF BOTH TEMPERATURE AND PRESSURE

When both temperature and pressure change, the effect on the volume may be determined by considering each separately. Thus, keeping pressure constant, calculate the effect of the change of temperature. Then, keeping the temperature constant, calculate the effect of change of pressure. These effects are illustrated by the following problem:

Example 1.—A certain weight of gas occupies 250 cc. at 20°C. and 700 mm. pressure. Calculate the volume that this gas will occupy at 5°C. and 740 mm. pressure.

If the pressure had remained constant, and only the temperature had changed, the effect would have been as follows:

$$20^{\circ}\text{C.} = 293^{\circ}\text{A.} \quad 5^{\circ}\text{C.} = 278^{\circ}\text{A.}$$

The temperature is lowered from 293°A. to 278°A. , causing the volume to decrease. Thus, *the original volume is multiplied by a fraction smaller than one*, or $250 \text{ cc.} \times \frac{278}{293} = 237.2 \text{ cc.}$ This volume of 237.2 cc. is the volume that the given weight of gas would occupy at the lower temperature (278°A.) if the pressure had remained the same, *i.e.*, 700 mm. However, the pressure is changed from 700 to 740 mm. This increase in pressure causes a further decrease in volume (Boyle's Law). Consequently, *the foregoing volume (237.2 cc.) must be multiplied by another fraction smaller than one*, or $(250 \text{ cc.} \times \frac{278}{293}) \times \frac{700}{740} = 224.3 \text{ cc.} = \text{the new volume under the new conditions of temperature and pressure.}$

Example 2.—A certain quantity of a gas measured 500 cc. at a temperature of 15°C. and 750 mm. pressure. What pressure

is required to compress this quantity of gas into a 400-cc. vessel at a temperature of 50°C.?

$$15^{\circ}\text{C.} = 288^{\circ}\text{A.} \quad 50^{\circ}\text{C.} = 323^{\circ}\text{A.}$$

The temperature is raised from 288°A. to 323°A. If the volume is kept constant, raising the temperature creates a rise of pressure; *i.e.*, this is the effect of the temperature change. Thus, *the original pressure must be multiplied by a fraction greater than one*, or it becomes 750 mm. $\times \frac{323}{288}$.

Now, at the higher temperature, 500 cc. of the gas is compressed to a volume of 400 cc. In order to accomplish this, the pressure must be *proportionately increased* (if temperature is kept the same); therefore, to take into account both effects, the pressure must be made $\frac{500}{400}$ of its former value to do this; thus, New pressure = $(750 \text{ mm.} \times \frac{323}{288}) \times \frac{500}{400} = 1,051.3 \text{ mm.}$ (See Table VII for pressure conversions.)

Example 3.—An expansion tank holds 2.5 cu. ft. of a gas at 72°F. and 30 in. of mercury. What temperature, expressed in degrees Fahrenheit, is required to cause the gas to expand to 3.0 cu. ft. at a pressure of 29.5 in. of mercury?

Keeping the temperature constant, the effect of decreasing the pressure from 30 to 29.5 in. of mercury is to increase the volume (Boyle's Law). Since $V \propto 1/P$, therefore,

$$2.5 \times \frac{30}{29.5} = 2.54 \text{ cu. ft. (at constant temperature)}$$

In order that 2.54 cu. ft. of gas at 72°F. may expand to 3.0 cu. ft. (pressure must remain constant), the temperature must increase (Gay-Lussac's Law).

$$72^{\circ}\text{F.} = 72^{\circ} + 460^{\circ} = 532^{\circ}\text{R.}$$

Since $V \propto T$ (at constant pressure), the ratios of volume to temperature may be expressed as follows:

$$\frac{2.54 \text{ cu. ft.}}{3.00 \text{ cu. ft.}} = \frac{532^{\circ}\text{R.}}{x^{\circ}\text{R.}}$$

or

$$x^{\circ}\text{R.} = \frac{532 \times 3}{2.54} = 628^{\circ}\text{R.}$$

and

$$628^{\circ} - 460^{\circ} = 168^{\circ}\text{F.}$$

The student will note that in solving the foregoing examples which involve changes in volume (and in density) of gases with variations in both temperature and pressure conditions, a "common-sense" method of attack has been employed. Generally students approach problems of this type equipped with the well-known combined gas-law formula (intentionally omitted here) presented to them in previous courses in chemistry and physics. Applying this formula by a mere substitution process leaves much to be desired with regard to development of the real thought process. Experience has shown that in many instances this "mathematical mill operation" fails the operator completely, resulting in confusion and loss of time, since fundamental knowledge of the development of this formula is lacking at the outset. In this text the use of the gas-law formula, by method of substitution, is definitely discouraged, and the student is admonished to reason out the problem from the facts presented similar to those presented in the foregoing examples.

The following outline is presented to serve as a working guide in solving problems dealing with volume changes with changes in temperature and pressure.

Step 1. Since the temperature T is to be expressed on the absolute scale, convert the given T in terms of degrees Kelvin ($^{\circ}\text{A.}$) or degrees Rankine ($^{\circ}\text{R.}$), as the case may be.

Step 2. Note whether the temperature is (a) increased or (b) decreased. If it is increased, applying Charles' or Gay-Lussac's Law, the volume is proportionately increased, and the given volume is multiplied by a fraction greater than unity. If the temperature is decreased, the volume will correspondingly decrease, and the given volume is multiplied by a fraction less than unity. Under either of these conditions of temperature change, the pressure is kept constant.

Step 3. Note the changes in pressure. (a) If pressure is increased, the new volume, under the new conditions of temperature, is multiplied by a fraction less than unity, with a subsequent decrease in volume. This, of course, is in accordance with Boyle's Law. Or (b) if the pressure is decreased, the new volume,

under the new temperature conditions, is multiplied by a fraction greater than unity, causing an increase in volume.

The combination of these steps is a much more rational solution of this type of problem and should create in the mind of the student a sense of personal satisfaction in this accomplishment.

EFFECT OF CHANGES IN PRESSURE AND TEMPERATURE ON THE DENSITY OF A GAS

We have noted that the volume of a gas is inversely proportional to the pressure. From this it can be seen that the **density of a gas is directly proportional to the pressure**. When a gas is compressed, the volume decreases proportionately. The weight remains the same; *i.e.*, the same weight of gas is caused to occupy a smaller volume. The density (mass per unit volume) is increased. Thus, suppose that the 900 cc. of gas (Fig. 7) in the cylinder weighs 4.5 g. The density is $4.5 \text{ g./}900 \text{ cc.} = 0.005 \text{ g./cc.}$, or 5 g./l.

When the volume is decreased to 450 cc. by doubling the pressure, the density becomes $4.5 \text{ g./}450 \text{ cc.} = 0.01 \text{ g./cc.}$, or 10 g./l. The total weight of the gas remains the same, 4.5 g.; therefore by doubling the pressure the density is doubled. Similarly, trebling the pressure would treble the density, etc.

As might be expected, changes in temperature also affect the density of gases. Everyone is familiar with the fact that in a warm room the air found close to the ceiling is warmer than that near the floor. Warm air has a lower density than cold air. Hence it rises.

Increase in temperature causes the volume of a gas to increase but does not change the mass. The *mass per unit volume*, *i.e.*, the density of the gas, will therefore decrease as the temperature is raised. However, the total weight of the gas remains the same. Stated otherwise, the **density of a gas varies inversely as the absolute temperature**.

The combined effect of changes of both temperature and pressure is illustrated in the solution of the following problem:

Example.—The density of helium is 0.1782 g./l. at S.T.P. Calculate the density of this gas at 25°C. and 740 mm. pressure.

As has been stated in Chap. I, the density of a gas is equal to its mass per unit volume expressed in grams per liter at S.T.P.

In the foregoing problem, then, the temperature is changed from 0°C. to 25°C. , and the pressure is decreased from 760 to 740 mm.

$$0^{\circ}\text{C.} = 273^{\circ}\text{A.} \quad 25^{\circ}\text{C.} = 298^{\circ}\text{A.}$$

The temperature is raised from 273°A. to 298°A. This will cause the density of the gas to decrease. It follows, then, that the density must be multiplied by a fraction smaller than one, or $0.1782 \times \frac{273}{298}$.

Now, simultaneous with this increase in temperature is a decrease in pressure which causes the density to become still smaller by a fraction $\frac{740}{760}$. (The density varies directly with pressure.)

The combined effect of changes in both temperature and pressure is then given by the following expression: $(0.1782 \times \frac{273}{298}) \times \frac{740}{760} = 0.1588 \text{ g./l.} =$ the density of helium at 25°C. and 740 mm.

PARTIAL PRESSURES

Consider two vessels as shown in Fig. 8, each containing 1,000 cc. of a different gas, each under a pressure P . If communication is established between the vessels by means of the stop-cock, in a short time it will be found that the gas from A has diffused into B and that that in B has diffused into A until the composition of the mixture of the two gases is the same at every point in either vessel. The 1,000 cc. of A has expanded until it occupies 2,000 cc. The 1,000 cc. of B has

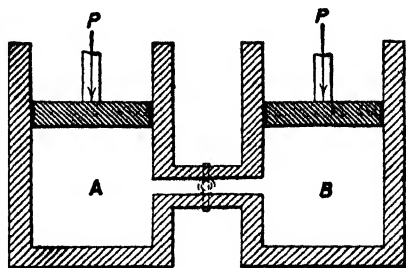


FIG. 8.

expanded until it occupies 2,000 cc. Since the volume of each gas has been doubled, the pressure acting upon it must have been halved (Boyle's Law). That is, the gas A is now under pressure $P/2$; likewise the gas B is under a pressure of $P/2$. The sum of the pressures on the two gases is then $P/2 + P/2$ which equals and balances the pressure P on the piston. If this were not the case, the piston would move down. Hence, the total pressure of

a mixture of gases may be regarded as the sum of the pressures that each would exert if it alone occupied the whole space. This is known as Dalton's Law of Partial Pressures.

VAPOR PRESSURE OF WATER

When a gas is collected over water at a given temperature (*i.e.*, the gas is in contact with liquid water), the stage is ultimately reached when the gas becomes saturated with water vapor; *i.e.*, a condition of equilibrium has been established. This water vapor in the gas, like any other gas, has a partial pressure of its own and at equilibrium exerts a maximum vapor pressure at the given temperature. This maximum vapor pressure at the given temperature is commonly called the vapor pressure of water. It is expressed in millimeters of mercury and varies with the temperature but always has the same value for the same temperature when the gas is saturated with water vapor.

When a gas is collected over water, the total pressure of the gas in the receiver consists of the sum of (a) vapor pressure of water and (b) the pressure of the gas itself. The actual pressure exerted by the gas alone (dry) is determined by subtracting the vapor pressure of water (millimeters of Hg) at the given temperature from the atmospheric pressure or the barometric pressure (millimeters of Hg) at the same temperature.

It is appropriate to mention at this point that when gases are collected over mercury, it is not necessary to make a correction for the vapor pressure of mercury at a given temperature. This is because of the exceedingly low vapor pressure of mercury at ordinary temperatures (less than 0.0002 mm. at 0°C., 0.008 mm. at 40°C., 0.270 mm. at 100°C.), and thus its influence as far as the partial pressure of mercury vapor is concerned is negligible.

Correction for Difference in Levels.—It is customary when collecting gases over water or mercury to adjust the receivers so that the level of the liquid inside the receiver is the same as that on the outside. Under these conditions the gas in the receiver will be under the same pressure as the atmosphere, *i.e.*, the barometric pressure. Where it is not possible to adjust the receiver so that the levels of the liquid will be the same, it is necessary to make a correction for this difference in levels. Consider that a gas is collected over mercury; if the mercury

inside the receiver is at a higher level than that on the outside, the pressure of the gas is less than atmospheric pressure by a column of mercury equal in height to the distance from the level inside the receiver to the level outside. On the other hand, if the mercury inside the receiver is at a lower level than that on the outside, the pressure of the gas is greater than the atmospheric pressure. The actual pressure of the gas will equal the atmos-

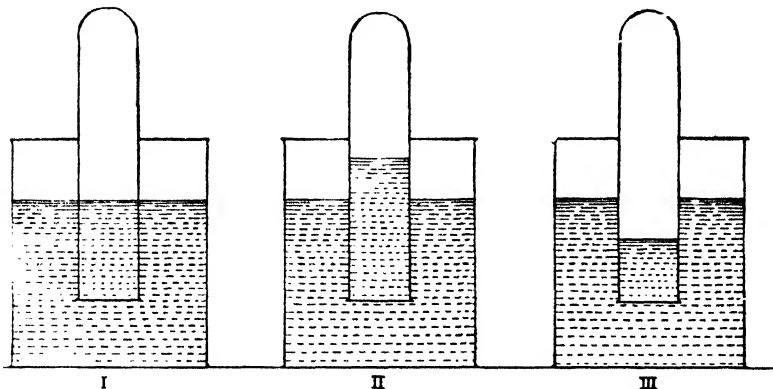


FIG. 9. I. Level of the liquid inside the tube at the same level as the liquid outside. II. Level of the liquid inside the tube higher than the level of the liquid outside. III. Level of the liquid inside the tube lower than the level of the liquid outside.

pheric pressure plus the pressure exerted by a column of mercury equal in height to the distance from the level outside the receiver to that on the inside.

If the gas is collected over water, the correction for difference in levels must also be made, as in the case where mercury is the liquid. The atmospheric pressure, however, is expressed in millimeters of Hg. In order to obtain the actual pressure of the gas over water in the container, the difference in levels of water in millimeters must be converted to the equivalence of millimeters of Hg.

Since mercury has a specific gravity of 13.59, then a column of water 50 mm. in height will exert a pressure equal to $1/13.59$ of 50, or 3.6 mm. of Hg. The correction for the difference in levels is made as stated above in the case of mercury.

Example.—A quantity of gas contained in a receiver and collected over water measured 130 cc. at a temperature of 22°C.

and a barometric pressure of 758 mm. The level of the water inside the receiver is 68 mm. above the outside level. The vapor pressure of water at 22°C. = 19.66 mm. of Hg. What volume will the dry gas occupy at standard conditions?

1. To correct for the difference in levels:

$$68 \text{ mm. of water} \approx \frac{68}{13.59}, \text{ or } 5 \text{ mm. of Hg}$$

$$758 \text{ mm.} - 5 \text{ mm.} = 753 \text{ mm.}$$

2. The vapor pressure of water at 22°C. = 19.66 mm. of Hg:

Then 753 mm. - 19.66 mm. = 733.34 mm., which is the actual pressure of the dry gas.

TABLE VIII.—VAPOR PRESSURE OF WATER IN MILLIMETERS OF MERCURY

t°C.	Pressure, mm. of Hg	t°C.	Pressure, mm. of Hg	t°C.	Pressure, mm. of Hg
0	4.6	21	18.5	60	149.4
1	4.9	22	19.7	70	233.7
2	5.3	23	20.9	80	355.1
3	5.7	24	22.2	90	525.8
4	6.1	25	23.5	95	633.9
5	6.5	26	25.0	96	657.6
6	7.0	27	26.5	97	682.1
7	7.5	28	28.1	98	707.3
8	8.0	29	29.8	99	733.2
9	8.6	30	31.6	99.2	738.5
10	9.2	31	33.4	99.4	743.8
11	9.8	32	35.4	99.6	749.2
12	10.5	33	37.4	99.8	754.6
13	11.2	34	39.6	100	760.0
14	11.9	35	41.9	100.2	765.4
15	12.7	36	44.6	100.4	770.9
16	13.6	37	47.1	100.6	776.4
17	14.5	38	49.7	100.8	782.0
18	15.4	39	52.4	101	787.5
19	16.4	40	55.3	105	906.1
20	17.4	50	92.5	110	1074.6

The gas measured 130 cc. at 22°C. and at a pressure that we have just determined amounts to 733.34 mm. Let us now calculate the volume that this gas will occupy if the temperature is

lowered to $0^{\circ}\text{C}.$ and the pressure raised to 760 mm., *i.e.*, if the gas is changed to standard conditions.

Since the temperature is lowered from $22^{\circ}\text{C}.$ ($295^{\circ}\text{A}.$) to $0^{\circ}\text{C}.$ ($273^{\circ}\text{A}.$), the volume (130 cc.) will be decreased $273/295 \times 130$ cc. if the pressure is constant (Gay-Lussac's Law). The pressure, however, is increased from 733.34 to 760 mm., which would further reduce the volume (Boyle's Law). Combining the two changes in one expression as previously explained in detail, we have $130 \text{ cc.} \times 273/295 \times 733.34/760 = 116.2 \text{ cc.}$, which is the volume at $0^{\circ}\text{C}.$ and 760 mm.

A table of the values of the vapor pressure of water (maximum vapor pressure) at temperatures ranging from $0^{\circ}\text{C}.$ to $100^{\circ}\text{C}.$ is given on page 40.

Problems

97. A volume of helium measuring 623 cc. at a pressure of 735.5 mm. is subjected to a pressure of 800 mm., the temperature remaining constant. What will be the new volume? *Ans.* 572.7 cc.
98. A gas occupying a volume of 500 cc. under a pressure of 745.5 mm. of Hg was allowed to expand until the volume measured 875 cc., the temperature remaining constant during the expansion. What pressure does the gas exert under the latter conditions? *Ans.* 426 mm.
99. Calculate the volume of oxygen if 345 cc. of the gas at $21^{\circ}\text{C}.$ is cooled to $-10^{\circ}\text{C}.$, pressure remaining constant. *Ans.* 308.6 cc.
100. If 100 cc. of a gas at $18^{\circ}\text{C}.$ is heated to a temperature of $30^{\circ}\text{C}.$, pressure remaining constant, what will be the new volume? *Ans.* 104.1 cc.
101. A volume of chlorine measuring 450 cc. is allowed to expand to a volume measuring 900 cc. at a constant temperature. The density of chlorine is 3.22 g./l. at S.T.P. Calculate the weight of 100 cc. of the expanded gas. *Ans.* 0.161 g.
102. The density of chlorine is 3.22 g./l. at S.T.P. At what pressure will 1 l. of this gas weigh 1 g., the temperature remaining constant at $0^{\circ}\text{C}.$? *Ans.* 236 mm.
103. At what temperature will 1 l. of oxygen weigh 1 g. if the pressure remains constant at 760 mm.? The density of oxygen is 1.429 g./l. at S.T.P. *Ans.* $117.1^{\circ}\text{C}.$
104. The density of carbon dioxide is 1.9766 g./l. at S.T.P. At what pressure will 1 l. of the gas weigh 1 g., the temperature remaining fixed at $0^{\circ}\text{C}.$? *Ans.* 384.49 mm.
105. A liter of air at standard conditions weighs 1.293 g. At what temperature will 200 cc. of air weigh 0.1 g., the pressure remaining fixed at 1 atm.? *Ans.* $432.9^{\circ}\text{C}.$
106. A volume of oxygen measuring 300 cc. at standard conditions was compressed until the volume was 130 cc., the temperature remaining

- constant. Calculate the weight of 30 cc. of the compressed gas. The density of oxygen is 1.429 g./l. at S.T.P. *Ans.* 0.0989 g.
107. A volume of chlorine measuring 500 cc. at standard conditions is heated to a temperature of 25°C., constant pressure being maintained during the expansion. Calculate the density of the expanded gas. The weight of 1 l. of chlorine at 0°C. and 760 mm. is 3.22 g.
Ans. 545.78 cc.; 2.94 g./l.
108. Calculate the weight of 1 l. of nitrogen collected at 21°C. and 750 mm. pressure. One liter of this gas at standard conditions weighs 1.25 g.
Ans. 1.145 g.
109. The density of chlorine is 3.22 g./l. at S.T.P. What weight of this gas is contained in a flask of 100 cc. capacity at a temperature of 24°C. and 750 mm. pressure?
Ans. 0.292 g.
110. Under standard conditions of temperature and pressure, 1 cu. ft. of hydrogen sulfide weighs 1.539 oz. Calculate the weight in ounces of the gas contained in a gasometer of 2.5 cu. ft. capacity at a temperature of 20°C. and a barometric pressure of 770 mm. *Ans.* 3.632 oz.
111. Calculate the temperature necessary to expand 200 cc. of a gas at 0°C. and 750 mm. pressure to a volume of 250 cc. at 740 mm. pressure.
Ans. 63.7°C.
112. A liter of hydrogen at 0°C. and 760 mm. pressure was subjected to a pressure of 20 atm., and the temperature increased to 120°C. Calculate the new volume.
Ans. 71.97 cc.
113. A gas occupying a volume of 333 cc. at 25°C. exerts a pressure of 750 mm. If the conditions are changed to -11°C. and 730 mm. pressure, what will be the volume?
Ans. 300.79 cc.
114. What pressure must be applied to a body of gas in order that its volume may measure 100 cc. at 21°C., when its volume at 18°C. and 758 mm. pressure is 250 cc.? *Ans.* 2.514 atm.
115. At a temperature of 21°C. and 745 mm. pressure, 1 l. of a gas weighs 0.9 g. What weight of the gas can be contained in a vessel of 200 cc. capacity if the conditions are changed to 10°C. and 755 mm. pressure?
Ans. 0.189 g.
116. Calculate the temperature necessary to reduce 250 cc. of dry air at 22°C. and 755 mm. pressure to a volume of 100 cc. at a pressure of 700 mm. *Ans.* -163.6°C.
117. A quantity of gas contained in a steel cylinder of 2-l. capacity weighed 4 g. under 200 atm. pressure and at 0°C. Calculate the density of this gas at 70°F. and 700 mm. pressure. *Ans.* 0.0085 g./l.
118. The density of chlorine is 3.22 g./l. at S.T.P. It was found that 1 l. of chlorine weighs 1.26 g. at a pressure of 775 mm. and a certain temperature. Calculate the temperature of the gas. *Ans.* 437.67°C.
119. A quantity of gas weighing 10 g. at 400 mm. pressure and -148°C. was heated to 300°C., and the pressure changed to 300 mm. Five hundred cubic centimeters of this rarefied gas was found to weigh 1.0 g. Calculate (a) the original volume of the gas; (b) the original density in grams per liter. *Ans.* (a) 818.06 cc.; (b) 12.22 g./l.

120. A quantity of chlorine is confined in a vessel of 50 cc. capacity at 80°C . and 800 mm. pressure. The density of chlorine is 3.22 g./l. at S.T.P. Calculate the weight of the gas in the vessel. *Ans.* 0.131 g.
121. Calculate the volume of nitrogen collected at a temperature of 77°F . and a pressure of 14.7 lb. per sq. in., required to fill 10 steel cylinders, each cylinder having a capacity of 2 cu. ft. and holding the gas under a pressure of 2,000 lb. per sq. in. at 70°F . *Ans.* 2,757 cu. ft.
122. Acetylene is obtainable in steel cylinders (holding 2.75 cu. ft.) which are packed with a porous filler saturated with acetone in which the acetylene is dissolved under a pressure of 250 lb. per sq. in. at 70°F . Calculate in cubic feet the volume of this gas necessary to fill one of these cylinders at 70°F . and 14.7 lb. per sq. in. pressure. *Ans.* 46.76 cu. ft.
123. Calculate the volume of hydrogen in cu. ft. at 68°F . and 14.7 lb. per sq. in. pressure required to fill 10 steel cylinders each holding 1.5 cu. ft. of gas and under a pressure of 1,800 lb. per sq. in. at 68°F . *Ans.* 1,836 cu. ft.
124. Calculate the number of steel cylinders each holding 200 cu. ft. of helium under a pressure of 1,800 lb. per sq. in. at 70°F . required to furnish sufficient helium to fill a dirigible of 2,500,000 cu. ft. capacity at a pressure of 14.7 lb. per sq. in. at 77°F . *Ans.* 100.6 cylinders.
125. A class of 275 students in qualitative analysis laboratory uses 1,400 cu. ft. of hydrogen sulfide gas under laboratory conditions (21°C . and 758 mm.) in one semester. This H_2S gas is obtained from liquid H_2S . One pound of liquid H_2S yields 4.68 cu. ft. of gaseous hydrogen sulfide under standard conditions. The liquid H_2S costs \$1 per pound. Calculate the cost per student for hydrogen sulfide gas in the laboratory for a semester. *Ans.* \$1.01 per student.
126. A volume of gas contained in a eudiometer (graduated tube) measured 70 cc. over mercury at a temperature of 21°C . and a barometric pressure of 755 mm. The level of the mercury inside the measuring tube was 35 mm. above that on the outside. What volume will the gas occupy at 30°C . and 760 mm. pressure? *Ans.* 68.34 cc.
127. A gas receiver contains 500 cc. of helium collected over mercury. The level of the mercury outside the tube is 50 mm. lower than that inside the tube. The temperature is 21°C ., and barometer reading 750 mm. What volume would this gas occupy at standard conditions? *Ans.* 427.6 cc.
128. What volume will 850 cc. of gas measured over water at 22°C . and 730 mm. pressure occupy at standard conditions? *Ans.* 735.1 cc.
129. A quantity of nitrogen collected in a vessel over water measured 500 cc. at a temperature of 25°C . and 755 mm. pressure. The level of the water inside the vessel was 4 in. above the outside level. Calculate the volume of the gas at standard conditions. *Ans.* 436 cc.
130. What weight of dry hydrogen is contained in 500 cc. of the gas measured over water at 22°C . and 743 mm. pressure? *Ans.* 0.0396 g.

- 131.** The density of oxygen is 1.429 g./l. at S.T.P. Calculate the weight of oxygen (dry) collected over water at 21°C. and 755 mm. pressure that will be contained in a vessel of 500 cc. capacity. *Ans.* 0.6587 g.
- 132.** Dry air contains, by volume, 78.03 per cent nitrogen, 20.9 per cent oxygen, 0.9 per cent argon, 0.04 per cent carbon dioxide. Calculate the partial pressure of each of these constituents at 758 mm. pressure. *Ans.* N₂, 591.46 mm.; O₂, 158.4 mm.; A, 6.8 mm.; CO₂, 0.3 mm.
- 133.** A 250-cc. flask was evacuated, and into it was forced 150 cc. of hydrogen under a pressure of 750 mm., 75 cc. of oxygen under a pressure of 350 mm., and 50 cc. of nitrogen under a pressure of 250 mm. Determine (a) the partial pressure of each gas after mixing; (b) the total pressure of the mixture. *Ans.* (a) 450 mm. for H₂, 105 mm. for O₂, 50 mm. for N₂; (b) 605 mm.
- 134.** A 300-cc. glass flask was evacuated, and into it was forced 50 cc. of hydrogen under a pressure of 400 mm., 180 cc. of oxygen under a pressure of 250 mm., and 85 cc. of nitrogen under a pressure of 700 mm. Calculate (a) the partial pressure of each gas after mixing, (b) the total pressure of the mixture. *Ans.* (a) 66.67 mm., 150.00 mm., 198.33 mm.; (b) 415.0 mm.
- 135.** Four liters of nitrogen is contained in a vessel under a pressure of 2.5 atm., and 6 l. of carbon dioxide is contained in another vessel under a pressure of 5 atm. Both gases are at a temperature of 20°C. The two gases are then transferred to a third vessel of 10 l. capacity, and during the transfer the gases are cooled to a temperature of 10°C. What is the pressure of the gaseous mixture in this vessel? *Ans.* 3.86 atm., or 2,933.6 mm. of Hg.

Additional Problems without Answers, for Quizzes

- 136.** The density of argon is 1.7809 g./l. at S.T.P. Calculate the weight of 1 l. of the gas at 21°C. and 750 mm. pressure.
- 137.** What volume will 40 cu. ft. of hydrogen measured at a pressure of 29 in. of mercury occupy under a pressure of 28 in. of mercury, temperature remaining constant?
- 138.** A flask can stand an internal pressure equivalent to 2,500 mm. of mercury. It is filled with a gas at 21°C. and 758 mm. pressure. Above what temperature will it burst?
- 139.** A volume of gas measuring 200 cc. at 200°C. and a pressure of 700 mm. was cooled to 2°C., and the volume increased to 400 cc. Calculate the new pressure.
- 140.** A gas occupying a volume of 200 cc. at 22°C. and a pressure of 200 mm. of mercury was cooled to 1°C., and the pressure increased to 3 atm. Calculate the new volume.
- 141.** A glass cylinder contains 2.15 g. of air at a pressure of 750 mm. of mercury. At what pressure will the cylinder contain 4.1 g. of air, temperature remaining constant?

142. Calculate the decrease in temperature necessary to reduce 370 cc. of argon at 21°C . and 755 mm. pressure to a volume of 200 cc. at a pressure of 745 mm.
143. A glass flask having a volume of 200 cc. is filled with helium at a pressure of 725 mm. at 21°C . The flask is heated to 200°C . Calculate the internal pressure on the flask.
144. A volume of gas measuring 700 cc. at 30°C . and 745 mm. pressure is compressed to a volume of 350 cc. at 20°C . Calculate the new pressure to which the gas must be subjected.
145. What pressure must be applied to a body of gas in order that its volume may measure 146.5 cc. at 21°C . when its volume at 15°C . and 751 mm. pressure measures 217.5 cc.?
146. Calculate the pressure that must be applied to a gas at a temperature of 18°C . in order that its volume may remain the same as it does under standard conditions.
147. A volume of gas weighing 8 g. was expanded, at constant temperature, until the pressure was reduced to one-half its former value. Five hundred cubic centimeters of the rarefied gas weighed 1.25 g. (a) What was the original volume of the gas? (b) Calculate the original density.
148. A volume of gas measured 64 cc. over mercury at a temperature of 75°F . and a barometer reading of 26.8 in. The level of the mercury inside the measuring tube was 3.9 in. above that on the outside. Calculate the volume of the gas at standard conditions.
149. A gasometer holds 500 cc. of a gas collected over water at 15°C . and 748 mm. pressure. What volume will the gas occupy at -15°C . and 760 mm. pressure when deprived of its moisture?
150. A volume of argon collected in a gasometer measures 500 cc. over water at 20°C . and 740 mm. pressure. Calculate the volume that the gas will occupy, dry (a) at 20°C . and 740 mm.; (b) at standard conditions.
151. A container holds 400 cc. of nitrogen collected over water at 25°C . and a pressure of 1 atm. The level of the water inside the container is 200 mm. above the level of the water outside. Calculate the volume of the gas, dry, at 0°C . and 760 mm. pressure.
152. A glass cylinder holds 500 cc. of a gas collected over water at a temperature of 15°C . and 758 mm. pressure. Calculate the volume of the gas, dry, when the conditions are changed to 20°C . and 745 mm. pressure.
153. Calculate the volume occupied by 10 g. of oxygen at 20°C . and 750 mm. pressure when collected over water.
154. Calculate the weight of hydrogen contained in a steel cylinder of 6.2 cu. ft. capacity, at 70°F . and 1,800 lb. per sq. in. pressure (22.4 cu. ft. of hydrogen, at S.T.P., weighs 2.016 oz.).
155. Calculate the weight of oxygen confined in a cylinder, 4 by $1\frac{1}{2}$ ft. diameter, at 21°C . and 744 mm. pressure (32 oz. of oxygen occupies 22.4 cu. ft., at S.T.P.).
156. A glass vessel contains 3.5 l. of CO_2 , and another vessel holds 5.5 l. of N_2 ; both gases are at the same temperature and under a pressure of

- 2.6 and 1.5 kg. per sq. cm., respectively. Both are now mixed together in a vessel having a capacity of 5 l. There is no change in temperature. Calculate the pressure of the mixture in the last vessel.
- 157.** Each of two glass vessels contains 5 l. of gas, one being under a pressure of 750 mm., and the other under a pressure of 730 mm., both gases kept at a temperature of 70°C. The two vessels are placed in communication with each other, and all the gas compressed into one of the vessels. During this operation the temperature is increased to 120°C. What will be the pressure of the gaseous mixture in this vessel?
- 158.** Given that 1 cu. ft. of hydrogen sulfide gas weighs 1.539 oz., at S.T.P. Calculate the weight of this gas contained in a gasometer of 5 cu. ft. capacity at a temperature of 22°C. and barometric pressure of 762 mm. of Hg.
- 159.** A flask while open to the air is heated from room temperature (21°C.) to 200°C., and the barometric pressure is 755 mm. The flask is then stoppered and cooled to 28°C. Calculate the final pressure in the flask.
- 160.** A steel cylinder contains 7.25 oz. of oxygen, measured at 70°F. and 1,500 lb. per sq. in. pressure. Calculate the volume of oxygen obtainable from the cylinder, at 75°F. and 29.7 in. of mercury (32 oz. of oxygen occupies 22.4 cu. ft., at S.T.P.).
- 161.** A steel cylinder contains 2.75 oz. of methane, measured at 70°F. and 1,200 lb. per sq. in. pressure. Calculate the volume of methane, at 72°F. and 1 atm., that can be obtained from one of these cylinders (16 oz. of methane occupies 22.4 cu. ft., at S.T.P.).

CHAPTER III

OUTLINE

Jean Rey observed that there is a limiting proportion of air that a metal will absorb on calcination.

A given weight of Mg will combine with a definite weight of oxygen but not with more and not with less.

In general, a definite weight of one element will combine with a definite weight of another.

When a mixture of 32.06 g. of S and 55.84 g. of Fe is heated, all the S and all the Fe combine. None of the S or of the Fe remains uncombined.

If a mixture of 32.06 g. of S and more than 55.84 g. of Fe is heated, some Fe remains uncombined.

If a mixture of 55.84 g. of Fe and more than 32.06 g. of S is heated, some S remains uncombined.

S and Fe combine in a definite proportion, 32.06 to 55.84 parts by weight.

The Law of Definite Proportions. When elements unite to form a compound, they do so in a definite proportion by weight.

A compound can often be prepared by several different methods. The compound always contains the same elements combined in the same proportions by weight, no matter which method was used to prepare it.

Dalton's explanation of the Law of Definite Proportions. Chemical combination consists in the union of atoms in simple combinations. Examples of this.

Modern theory of atomic structure: structure of simple atoms; valence; polar bond; nonpolar bond.

Significance of the chemical formula.

Gram-atomic weight; gram-molecular weight; ways of expressing these weights in various quantity units.

THE LAW OF DEFINITE PROPORTIONS

Jean Rey in 1630 noted that when a metal was heated for some time in the air "the weight of the metal increased from the beginning to the end, but when the metal is saturated it can take up no more air. . . . Do not continue the calcination [heating] in this hope; you will lose your labor."

Experiments like the following illustrate this: When 24.32 g. of magnesium is heated in a porcelain crucible, exposed to the

air, a white powder results. The weight of this powder is greater than the original weight of magnesium, 24.32 g. We say that the magnesium has combined chemically with the oxygen of the air to form the white powder called magnesium oxide. The weight of the white powder is found to be 40.32 g. If the powder continues to be heated in the air, additional heating causes no further change in weight. We decide from this experiment that 24.32 g. of magnesium, when all of it is converted to the white powder, will unite with 16 g. of oxygen—**not more**—no matter how much oxygen surrounds it or how long the heating is continued. Magnesium and oxygen, therefore, combine in definite proportions of 24.32 parts by weight of magnesium to 16.00 parts by weight of oxygen to form the new substance.

Furthermore, it has been observed a great many times by other chemists that when magnesium unites with sulfur or when iron unites with sulfur or, in fact, when any element unites with any other or others, a definite weight of the one element always unites with a definite weight of the other and forms a definite weight of the new substance. The elements unite in **definite** proportions by weight to form the new substance.

To illustrate this further: Iron and sulfur can be mixed together in any proportions. From this mixture the iron could be separated by means of a magnet. The sulfur could be dissolved from the mixture by carbon disulfide.

If, however, the finely ground mixture of iron and sulfur is heated, say over a Bunsen flame, iron and sulfur combine chemically to form a new substance, iron sulfide. This substance has new properties, different from those of iron or of sulfur. We find that the iron and the sulfur combine to form this new substance in the proportion of 32.06 parts by weight of sulfur to 55.84 parts by weight of iron. Thus, if a finely ground mixture of 32.06 g. of sulfur and 55.84 g. of iron is carefully heated, they will combine completely. If we powder the mass after heating and examine it, we shall find^a that none of the iron remains uncombined. All the iron has united with the sulfur. Similarly, we shall find that **all** the sulfur has combined with the iron. None remains. Carbon disulfide will not remove any of it. We know, then, that iron and sulfur unite in the proportion of 55.84 parts by weight of iron to 32.06 parts by weight of sulfur.

If we heat a mixture of 32.06 g. of sulfur and, say, 165.00 g. of iron (more than 55.84 g.), not all the iron combines with the sulfur to form ferrous sulfide. We would find that 109.16 g. of iron would be left uncombined and retaining its original properties. The rest, 165.00 g. — 109.16 g., or 55.84 g. of iron, had united with the 32.06 g. of sulfur. This is the same proportion in which they united when all the sulfur and all the iron combined. We see, then, that iron and sulfur combine in the proportion of 32.06 parts by weight of sulfur with 55.84 parts by weight of iron, no matter whether more iron is present or not. Excess iron is left uncombined.

In the same way if we carefully heat a mixture of 55.84 g. of iron with, say, 250.00 g. of sulfur, instead of 32.06 g., we would find that only 32.06 g. of the sulfur united with the 55.84 g. of iron. The remainder, 250.00 g. — 32.06 g., or 217.94 g. of sulfur, would be left uncombined. Again, we see that iron and sulfur unite in the proportion of 55.84 parts by weight of iron to 32.06 parts by weight of sulfur, despite the fact that more sulfur was present. Sulfur and iron then combine in a definite proportion of 32.06 parts to 55.84 parts by weight.

From a great many observations like these which showed in every case that the elements combine in a definite proportion by weight, the underlying law has been deduced. It is known as the *Law of Definite Proportions*. **When elements unite to form a compound, they do so in a definite proportion by weight.**

ANOTHER WAY OF STATING THIS LAW

Very often a compound can be made by several different methods; but no matter what method is used, we find that the elements combine chemically in the same proportions by weight.

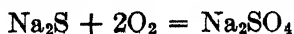
We usually find this by breaking up the compound into the elements by chemical means. This process is known as *analysis*.

Let us consider an example. Sodium sulfate may be prepared in several ways:

A. By the oxidation of sodium sulfide.

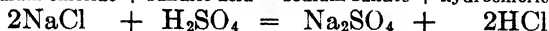


This reaction is represented by the chemical equation



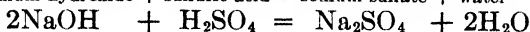
B. By treating some sodium salts with H_2SO_4 .

Sodium chloride + sulfuric acid = sodium sulfate + hydrochloric acid



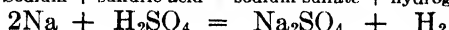
C. By treating sodium hydroxide with sulfuric acid.

Sodium hydroxide + sulfuric acid = sodium sulfate + water



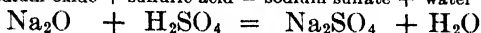
D. By treating sodium with sulfuric acid.

Sodium + sulfuric acid = sodium sulfate + hydrogen



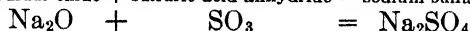
E. By treating sodium oxide with sulfuric acid.

Sodium oxide + sulfuric acid = sodium sulfate + water



F. By treating sodium oxide with SO_3 , the anhydride of H_2SO_4 .

Sodium oxide + sulfuric acid anhydride = sodium sulfate



If we examine the sodium sulfate made by any one of these methods, we find that it is identical in composition and properties with that made by any of the other methods; that it is always composed of three elements, sodium, sulfur and oxygen; and that **the relative weights of each present are always the same:**

46.00 parts by weight of sodium

32.06 parts by weight of sulfur

64.00 parts by weight of oxygen

in 142.06 parts by weight of sodium sulfate

We can then express the Law of Definite Proportions: **A definite chemical compound always contains the same elements combined in the same proportions by weight.**

ATOMIC THEORY EXPLANATION OF THIS LAW

The question now comes up, **Why** is it that the elements always combine in **exactly** the same proportions by weight in a given compound? A satisfactory explanation for this is found in the atomic theory offered by Dalton in 1802. While working with two compounds that led to the principle of multiple pro-

portions, Dalton conceived the ideas on which the present *Atomic Theory of Matter* is based.

The fundamental concept of this theory follows:

(a) All elements are made up of small particles called *atoms*. The atoms are real particles of matter that are chemically indivisible.

(b) All *atoms* of the *same element* have the *same weight*.

(c) *Atoms* of *different elements* have *different weights*.

(d) Chemical compounds are formed by the union of atoms of different elements: 1 atom of one element with 1 atom of another element; 1 atom of an element with 2 atoms of another; or 1 with 3; 2 with 2; 2 with 3; 3 with 2; 2 with 4; etc.

Since atoms and molecules are too small to be seen by the highest powered microscope, it is no wonder that we do not know the *actual weight* of an atom of any element. The actual weights of atoms have been calculated from reliable observations and are known to be extremely small numbers; thus, the weight of an atom of hydrogen is approximately 0.000,000,000,000,000,000,001,66 g. (1.66×10^{-24} g.). The **relative weights** of the atoms of all the elements have been accurately determined. They are spoken of as **atomic weights**. Thus, it is a fact that oxygen is 15.88 times as heavy as hydrogen. If we take the weight of an atom of hydrogen as 1, then the weight of an oxygen atom is 15.88. It is more convenient to take the weight of an oxygen atom as 16.00; then the weight of an atom of hydrogen is 1.008. *The relative weights of all the atoms or atomic weights are all determined on the basis of oxygen being equal to 16.00.* A table of the atomic weights of the elements is given on the inside of the front cover.

Although still well grounded in principle, Dalton's theory has been extended, as the result of recent advances in physical science. From studies of the phenomena of electrical discharge of gases in vacuum tubes and radioactivity, scientists have discovered that the atom is composed of equal quantities of positive and negative electricity. The following brief statements will present the essential details of the modern theory of atomic structure:

a. All atoms (except hydrogen) are composed of **protons** (unit of positive electricity), **electrons** (unit of negative elec-

tricity), and **neutrons** (neutral particle made up of a very closely situated proton-electron pair).

b. Each atom has a **nucleus** in which are groups of protons and neutrons (hydrogen excepted). The radius of the hydrogen nucleus or proton is of the order 10^{-13} cm., and the nucleus constitutes nearly all the mass of the atom.

c. Outside the nucleus, at relatively large distances from it, are a sufficient number of electrons arranged in shells or energy levels equal to the number of protons in the nucleus, which, of course, makes the atom electrically neutral.

d. The hydrogen atom is the simplest atom known. Its nucleus contains one proton and no neutrons. The one lone electron vibrates about this proton, thereby making the atom electrically neutral. The nuclei of all other atoms are made up of both protons and neutrons, thus accounting for the positive charge on these nuclei. This positive charge, in turn, is neutralized by a number of electrons outside the nucleus equal to the nuclear charge. The number of protons in the nucleus is called the **atomic number** of the element and symbolized by Z . It is also true that the **atomic number** corresponds to the number of electrons outside the nucleus. Thus, the atomic number of hydrogen, the lightest atom, is $1(Z = 1)$; and that of the heaviest atom, uranium, $Z = 92$.

e. The weight of an electron is about $1/1,845$ of the weight of the hydrogen atom and thus is negligible. Since a proton is a hydrogen atom that has lost an electron or is a hydrogen nucleus, commonly called a hydrogen ion, H^+ , the weight of a proton is very nearly the weight of a neutral hydrogen atom (atomic weight = 1.0078). The neutron, or proton-electron pair, has a weight of about 1.006 units, which is less than the atomic weight of hydrogen. This decrease in weight is supposed to be due to a *packing effect*. In fact, a neutron is said to be a "collapsed hydrogen atom."

f. Regarding the arrangement of the electrons, it has been shown that they are disposed in shells or various energy levels about the nucleus. From a chemical viewpoint, the *outermost electron shell* is of prime importance. It is only the electrons in this outermost shell that are free to leave or enter the atom when proper circumstances arise. Properties such as **valence**

and **chemical reactivity** in general are dependent upon the number and arrangement of electrons in the outermost shell, or valence shell, and are called **valence electrons**. The remainder of the atom, consisting of the nucleus (protons + neutrons) and the remainder low-lying shells, may be termed the *core* of the atom.

STRUCTURES OF SOME SIMPLE ATOMS

As previously stated, the hydrogen atom is the simplest atom, $Z = 1$. It consists of one proton in the nucleus and one electron outside the nucleus. Conceivably this atom can lose its electron under proper conditions and thus form a proton or a hydrogen ion, H^+ . The next lightest element is helium, with an atomic number of 2 ($Z = 2$) and an atomic weight of 4.002 ($A = 4.002$). This tells us that there are 2 protons in the nucleus and 2 electrons outside. To determine the number of neutrons in the nucleus, it is necessary only to subtract the atomic number Z from the atomic weight A , which in this case gives 2 neutrons. The 2 protons and 2 neutrons in the nucleus account for the atomic weight of 4. *The helium atom has the most stable arrangement of electrons of all the elements* and has no tendency to lose, gain, or share electrons with other atoms. Incidentally, the other chemically inert gases, neon ($Z = 10$), argon ($Z = 18$), krypton ($Z = 36$), xenon ($Z = 54$), are characterized by having stable electron arrangements. The lithium atom ($Z = 3$ and $A = 6.94$) is made up of 3 protons and 4 neutrons in the nucleus (accounting for an atomic weight of about 7) and 3 outside electrons. The electron arrangement of the lithium atom is such that the first shell, being very small in dimensions, contains only 2 electrons, and the third electron is located in a second shell outside the inner shell and at some distance away from the nucleus and its influence. Thus, this outermost, or valence, electron is rather easily lost, and lithium readily combines chemically with other atoms.

In like manner it is possible to picture heavier elements with correspondingly more complex electron arrangements. However, it should be noted that as the second shell builds up with 8 electrons, we have the structure of neon ($Z = 10$). Continuing with the addition of a second octet of electrons in the third shell,

the structure of argon ($Z = 18$) is formed. The third shell may build up with a total of 18 electrons; the fourth, with 32; and so on. When the first three shells have their full quota of electrons, *viz.*, 2, 8, and 18 electrons, respectively, and 8 electrons are contained in the fourth shell, we have the stable electron grouping of the krypton atom ($Z = 36$). Since the atomic weight of krypton is 83.7, the nucleus of this atom would contain 36 protons plus 48 neutrons.

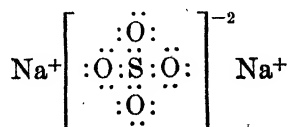
Chemical inertness is definitely associated with a symmetrical or stable electron configuration which characterizes the inert gases. Thus, it can be stated that when atoms combine or react with themselves to form molecules, or when atoms of one element combine with atoms of another element, they tend to revert to structures with stable or symmetrical electron groupings. In order to accomplish these structure conversions, it is well to consider the mechanism of chemical reaction. The chemical reactivity of an element depends upon the tendency of the atoms of that element to lose, gain, or share valence electrons; and in so doing, the atoms form structures with stable electron configurations. Since the outermost electrons of atoms are concerned with chemical reactivity, we can state that **valence** is the power that atoms possess to enter into chemical combination.

As a simple chemical combination, the union of a metal and a nonmetal to form a compound is exemplified in the reaction between sodium ($Z = 11$) and chlorine ($Z = 17$) to form the salt sodium chloride. The sodium atom having one valence electron tends to give up this electron and revert to the stable electron grouping of the neon structure ($Z = 10$), thereby becoming a positively charged *sodium ion*, Na^+ . On the other hand, the chlorine atom possesses 7 valence electrons and thus needs only one more to assume the electron grouping of the argon structure ($Z = 18$). Thus the chlorine atom, in gaining 1 electron, becomes a negatively charged ion and is commonly called the *chloride ion*, Cl^- . The combination of these events—the giving up of one electron by the sodium atom, forming the sodium ion, Na^+ , and the acceptance of this electron by the chlorine atom, thereby becoming a chloride ion, Cl^- —constitutes the chemical union of sodium and chlorine to form sodium

chloride. The two oppositely electrically charged ions are held together by an electrostatic force, or bond. To realize that this is undoubtedly the true mechanism in this type of reaction, one need only consider the facts that crystalline sodium chloride is definitely made up of tiny unit crystals in which sodium ions and chloride ions occupy alternate positions, 2.814 Å. apart, in a three-dimensional lattice framework, or space lattice. If solid sodium chloride is fused and subsequently electrolyzed, it will be found that the sodium ion migrates to the negative electrode, the cathode, and that chlorine is evolved at the positive electrode, the anode. It should be emphasized that in the formation of compounds in which the valence bond between atoms is brought about by the *transfer of electrons*, the bond is known as a **polar bond**, or an **ionic bond**.

Another method in which the valence electrons of atoms play a different role from that just described in exhibiting chemical reactivity is exemplified in the following: Consider the simplest of all atoms, the hydrogen atom. Atomic hydrogen, as such, does not exist under ordinary conditions of temperature and pressure. It is extremely reactive and unstable. The atoms of hydrogen actually unite with each other to form molecules of hydrogen, H_2 , with the simultaneous production of extremely high temperatures. This is the process involved in the operation of the atomic hydrogen torch so much used in modern welding of metals. In reacting with itself to form hydrogen molecules, H_2 , the *electrons* from each of the hydrogen atoms are *shared equally between two atoms*. This process of *sharing pairs of electrons* between atoms is a type of *valence bond* called a **covalent bond**, or a **nonpolar bond**.

In the formation of sulfuric acid and its salts, such as sodium sulfate, Na_2SO_4 , we find that both types of valence bonds prevail simultaneously. Thus, the structure of Na_2SO_4 may be represented by



Here the sodium ion, Na^+ , is joined to $(SO_4)^{-2}$ by a polar bond,

whereas the $(\text{SO}_4)^{-2}$ radical is held together by a nonpolar or covalent bond, the electrons being represented by dots. The charge on the radical is -2 . This is due to its having a total of 32 electrons shared between the sulfur and oxygen atoms, which is 2 more than the number present in 1 sulfur atom and 4 oxygen atoms. These 2 extra electrons are acquired from 2 sodium atoms, each of which is capable of releasing 1 electron.

It has been shown that molecules in which the atoms possess a definite electrical charge are held together by an electrostatic force, or polar bond. *The number of charges on an atom or radical in a compound is known as its valence number.* As an example; Lithium fluoride is a typical polar molecule, LiF. The valence number of lithium is $+1$, this atom having lost 1 electron, and the valence number of fluorine is -1 , this atom having gained 1 electron. These numbers, obviously, are the number of charges on each of these atoms in this compound.

Atoms that share electrons with other atoms have no definite electrical charge. The term valence number is truly not significant when dealing with nonpolar molecules. However, *a pair of shared electrons is known as one valence bond* and thus, in *nonpolar molecules*, represents **one unit of valence**. It is convenient to speak of positive and negative valence numbers of atoms in nonpolar compounds. Usually the positive valence number is assigned to those elements which exhibit electropositive characteristics and to the metals. The negative valence number is assigned to the elements that show electronegative tendencies and to the nonmetals. Thus, in the nonpolar molecule carbon tetrachloride, CCl_4 , the carbon exhibits a valence number of $+4$; and the chlorine, a valence number of -1 .

It is essential to assign the correct valence numbers to each element in a compound. It should be emphasized that, in every chemical compound, *the sum of positive valence numbers must equal the sum of the negative valence numbers* of the various atoms in the compound in order that *the molecule may be electrically neutral*. Thus, in sodium sulfate, Na_2SO_4 , the valence number of Na is $+1$, or a total of $+2$, and the radical (SO_4) is -2 . In considering the $(\text{SO}_4)^{-2}$, as each oxygen possesses a valence number of -2 or a total of -8 , the S atom must be assigned a valence number of $+6$. The algebraic sum of these total

valence numbers, of course, is zero. This can be represented by

$$\frac{\text{Na}_2^+ \text{S}^{+6} \text{O}_4^{-2}}{+2 + 6 \quad -8}.$$

In beginning his study of chemistry the student first learns of the existence or discovery of the 92 elements. He then becomes familiar with the language of chemistry by first memorizing the "chemical alphabet" which, of course, consists of the symbols for the various chemical elements. Then follows the task of memorizing the valence numbers of the common elements. The valence number, to be sure, has been previously explained to him as "the number of charges on an atom or radical in a compound." He is also told that atoms—the units of chemical exchange—ordinarily do not lead an independent existence but generally combine with themselves or other atoms to form molecules of various substances. Furthermore, these atoms and radicals are held together by forces that are either polar bonds or nonpolar bonds in the formation of chemical compounds. Then the system of chemical nomenclature is introduced, and the student learns the significance of the chemical formula—a sort of shorthand expression for a chemical compound. Thus he is told that the formula for sulfuric acid is H_2SO_4 , for ammonium nitrate NH_4NO_3 , and so on. Following this preliminary background, the fundamental laws and principles of chemistry are presented with various applications. Now we may ask; "Just what does a chemical formula stand for?" The following will briefly answer this question:

(a) The formula (through the use of symbols) tells us the elements that go to make up a given chemical compound or its composition. (b) The numbers of atoms of each element in one molecule of the compound are indicated by the small subscript numbers. (c) The formula furnishes us with the means of expressing the relative weight of the molecule, or the sum of the relative weights or atomic weights of the atoms in it, which is familiarly known as the **molecular weight**. It can also be said that the formula represents **1 gram-molecular weight** of a substance. (d) In the case of gases, we shall see later (Chap. V) that the formula represents a definite volume of a gas under standard conditions of temperature and pressure (0°C. and 760 mm. of Hg), S.T.P.

As indicated in this chapter, sodium sulfate may be formed in several ways, but we know that the sodium sulfate produced consists in every case of 2 atoms of sodium united with 1 atom of sulfur and 4 atoms of oxygen. Using the symbols for each element, this is represented by the formula $\text{Na}_2\text{S}_1\text{O}_4$, or simply Na_2SO_4 , one atom of an element being represented by the symbol for the element without any subscript.

To determine the molecular weight of a molecule of sodium sulfate, it is necessary to consider the following facts: Since the atomic weight is not an actual weight of an atom but a relative weight (on a basis of $\text{O} = 16$); and since the atomic weight of an element is proportional to the actual weight of an atom of that element, it is customary to express the atomic weight in grams, which is commonly called **gram-atomic weight**, or simply **one gram-atom**. The gram-atom contains a definite number of atoms which is the same for all elements, *viz.*, 6.06×10^{23} , known as the *Avogadro number*. Thus, 1 gram-atom of sodium is 22.997 g. of sodium; 2 gram-atoms of sodium is 2×22.997 g. or 45.994 g. of sodium; and so on. This leads us to the term **gram-molecular weight**. The molecular weight of a compound is the sum of the total atomic weights of all the atoms in it. It follows that the *sum of the gram-atomic weights of the atoms in a compound is known as the gram-molecular weight* of that compound. The gram-molecular weight is conveniently referred to as a **gram-mol** (g.-mol) and will be so symbolized throughout this text. Thus, 1 gram-mol of sodium sulfate contains:

$$\begin{array}{rcl}
 2 \text{ g.-atoms of Na} & = & 2 \times 22.997 = 45.994 \text{ g. of Na} \\
 1 \text{ g.-atom of S} & = & 1 \times 32.06 = 32.06 \text{ g. of S} \\
 4 \text{ g.-atoms of O} & = & 4 \times 16.00 = 64.00 \text{ g. of O} \\
 \hline
 1 \text{ g.-mol of Na}_2\text{SO}_4 & & = 142.054 \text{ g. of Na}_2\text{SO}_4
 \end{array}$$

It is a definite fact that the atomic weight ratios of Na, S, and O in 142.06 parts by weight of sodium sulfate are always exactly in the proportion 45.994:32.06:64.00. If the atoms united in some other ratio, the compound would not be sodium sulfate but some other substance and would, of course, possess entirely different properties from those possessed by sodium sulfate. We shall find (see next chapter) that some elements have the power to combine with one another in several different ways,

different substances being formed in each case. The proportions in which they combine are, however, definite in each case—definite for each different substance.

Thus far we have considered atomic weight units in the metric system—gram-atoms and gram-mols. It frequently becomes necessary to deal with the U. S. A. system of weights, and such terms as ounce-mol (oz.-mol), pound-atom (lb.-atom), and pound-mol (lb.-mol) come into being, particularly in industry. One ounce-mol of a compound can be defined as the sum of the ounce atomic weights (atomic weights expressed in ounces) of the atoms in that compound. Likewise, 1 pound-mol of a compound is a quantity represented by the sum of the pound-atomic weights of the atoms in that compound. The formula weight of a compound (relative weight) can be conveniently expressed in any unit of quantity in any system of measures as: gram-mol; kilogram-mol; ounce-mol; pound-mol; ton-mol. A few examples will be apropos at this stage to illustrate the use of these various quantity units and will also serve to illustrate the application of one of the most fundamental laws of chemistry—the Law of **Definite Proportions**.

Example 1.—How many grams of sulfur are contained in 2 gram-mols of sodium bisulfite?

The formula for sodium bisulfite is NaHSO_3 . This tells us that 1 gram-atom of S is contained in 1 gram-mol of NaHSO_3 . Since 1 gram-atom of sulfur contains 32.06 g. of S, then 2 gram-atoms of S, or 2×32.06 g. = 64.12 g. of S, is contained in 2 gram-mols of NaHSO_3 .

Example 2.—What weight of sulfur is there in 10 g. of sodium sulfate?

The formula for sodium sulfate is Na_2SO_4 . There are 142.06 g. of Na_2SO_4 contained in 1 gram-mol of Na_2SO_4 . Ten grams of Na_2SO_4 will contain $10/142.06$, or 0.0703 gram-mol of Na_2SO_4 .

Since 1 gram-mol of Na_2SO_4 contains 1 gram-atom of S, or 32.06 g. of S, 0.0703 gram-mol of Na_2SO_4 will contain 0.0703×32.06 , or 2.253 g. of S.

Example 3.—What weight of sulfur trioxide, SO_3 , is there in 10 g. of sodium sulfate?

Groups of elements can be considered just the same as elements on the foregoing principle. One gram-mol of Na_2SO_4

contains 1 gram-mol of SO_3 . Ten grams of Na_2SO_4 contains $10/142.06 = 0.0703$ gram-mol of Na_2SO_4 . Then

0.0703 gram-mol of Na_2SO_3 contains 0.0703 gram-mol of SO_3 .

1 gram-mol of Na_2SO_3 contains 80.06 g. SO_3 .

0.0703 gram-mol of SO_3 will contain 0.0703×80.06 , or 5.63 g. of SO_3 .

Example 4.—Calculate the percentage of phosphorus in calcium phosphate.

The formula for calcium phosphate is $\text{Ca}_3(\text{PO}_4)_2$.

1 gram-mol of $\text{Ca}_3(\text{PO}_4)_2$ contains 2 gram-atoms of P.

1 gram-mol of $\text{Ca}_3(\text{PO}_4)_2 = 310.28$ g. of $\text{Ca}_3(\text{PO}_4)_2$.

2 gram-atoms of P = $2 \times 31.02 = 62.04$ g. of P.

Then 310.28 g. of $\text{Ca}_3(\text{PO}_4)_2$ contains 62.04 g. of P.

1 g. of $\text{Ca}_3(\text{PO}_4)_2$ contains $\frac{1}{310.28} \times 62.04$ g. of P.

Since percentage means parts in one hundred parts (grams in 100 g., pounds in 100 lb., and so forth),

100 g. of $\text{Ca}_3(\text{PO}_4)_2$ will contain $100 \times 62.04/310.28$ g. = 19.99 g. of P, or 19.99 per cent of phosphorus.

Example 5.—Calculate the percentage purity of a sample of silver chloride ore that contains 65 per cent of Ag.

Silver chloride has the formula AgCl . One gram-mol of AgCl contains 1 gram-atom of Ag.

In 1 g.-mol of AgCl there is 143.34 g. of AgCl .

In 1 g.-atom of Ag there is 107.88 g. of Ag.

Since 143.34 g. of pure AgCl contains 107.88 g. of Ag, 100 g. of pure AgCl would contain $100 \times 107.88/143.34$ g. = 75.26 g. Ag. In other words, pure AgCl contains 75.26 per cent of Ag.

The silver chloride ore under consideration contains only 65.00 per cent of Ag. It contains, therefore, only $65.00/75.26$ as much Ag as it would if the ore were composed wholly of AgCl .

Sixty-five parts in 75.26, or $65.00/75.26$, is 0.8638 part in 1 part, is 100×0.8638 , or 86.38 parts in 100 parts, is 86.38 per cent. That is, the ore is 86.38 per cent pure. It contains 86.38 per cent of AgCl and $100.00 - 86.38$, or 13.62 per cent of something else.

Example 6.—Determine the theoretical amount in pounds of lead chromate, PbCrO_4 , that can be obtained from 1 ton of chromite ore which analyzed 28.5 per cent Cr_2O_3 .

It is evident from the chemical formulas Cr_2O_3 and PbCrO_4 that 1 pound-mol of Cr_2O_3 will yield 2 pound-mols of PbCrO_4 , since 2 atoms of Cr are available from Cr_2O_3 , and PbCrO_4 contains only 1 atom of Cr. This is conveniently represented by $1\text{Cr}_2\text{O}_3 = 2\text{PbCrO}_4$.

The chromite ore contains 28.5 per cent Cr_2O_3 . This means, of course, that 100 lb. of chromite contains 28.5 lb. of Cr_2O_3 .

1 lb. of chromite contains $\frac{1}{100} \times 28.5 \text{ lb.} = 0.285 \text{ lb. of } \text{Cr}_2\text{O}_3$.

Then 2,000 lb. (1 ton) of chromite will contain $2,000 \times 0.285 = 570.0 \text{ lb. of } \text{Cr}_2\text{O}_3$.

Since 152.02 lb. of Cr_2O_3 is contained in 1 pound-mol of Cr_2O_3 , 570.0 lb. of Cr_2O_3 will be contained in $570.0/152.02$ pound-mols of Cr_2O_3 , or 3.749 pound-mols of Cr_2O_3 . Now,

1 pound-mol of Cr_2O_3 yields 2 pound-mols of PbCrO_4 .

3.749 pound-mols of Cr_2O_3 will yield $3.749 \times 2 = 7.498$ pound-mols of PbCrO_4 .

1 pound-mol of PbCrO_4 contains 323.23 lb. of PbCrO_4 .

7.498 pound-mols of PbCrO_4 will contain $7.498 \times 323.23 = 2,423.58 \text{ lb. of } \text{PbCrO}_4$.

Problems

- 162.** Find the molecular weight of each of the following compounds: (a) crystallized sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; (b) calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$; (c) sodium chlorate, NaClO_3 ; (d) basic cupric carbonate, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

Ans. (a) 286.15; (b) 162.09; (c) 106.45; (d) 344.72.

- 163.** Determine the molecular weight of each of the following compounds: (a) silver tartrate, $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$; (b) sodium fluosilicate, Na_2SiF_6 ; (c) crystallized sodium sulfate (Glauber's salt), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; (d) basic lead carbonate (white lead), $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$.

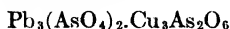
Ans. (a) 363.79; (b) 188.05; (c) 322.21; (d) 775.67.

- 164.** What is the molecular weight of each of the following: (a) crystallized ferrous sulfate (copperas), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; (b) crystallized sodium ammonium hydrogen phosphate (microcosmic salt), $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$; (c) basic mercuric carbonate, $2\text{HgO} \cdot \text{HgCO}_3$; (d) ferric ferrocyanide (Prussian blue), $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$?

Ans. (a) 278.02; (b) 209.12; (c) 693.83; (d) 859.02.

165. (a) How many parts by weight of mercury are there in 232.66 parts by weight of cinnabar, HgS ? (b) How many parts by weight of mercury are there in 100 parts by weight of cinnabar? (c) What is the percentage of Hg in cinnabar? *Ans.* (a) 200.6; (b) 86.22; (c) 86.22 per cent.
166. (a) How many parts by weight of sulfur are there in 87.9 parts by weight of ferrous sulfide? (b) How many parts by weight of sulfur are there in 100 parts by weight of ferrous sulfide? (c) What is the percentage of sulfur in ferrous sulfide?
Ans. (a) 32.06; (b) 36.47; (c) 36.47 per cent.
167. (a) How many parts by weight of calcium and of water are there in 219.086 g. of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$? (b) What is the percentage of calcium and of water in $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$?
Ans. (a) Ca , 40.07; H_2O , 108.096.
(b) Ca , 18.24 per cent; H_2O , 49.34 per cent.
168. (a) How many parts by weight of sulfur trioxide, SO_3 , are there in 233.43 parts by weight of BaSO_4 ? (b) What is the percentage of SO_3 in BaSO_4 ?
Ans. (a) 80.06; (b) 34.29 per cent.
169. (a) How many grams of magnesium and of phosphorus are there in 222.72 g. of $\text{Mg}_2\text{P}_2\text{O}_7$? (b) Calculate the percentages of magnesium and of phosphorus in $\text{Mg}_2\text{P}_2\text{O}_7$.
Ans. (a) 48.64 g. Mg ; 62.08 g. P .
(b) 21.83 per cent Mg ; 27.87 per cent P .
170. What is the percentage of carbon in (a) carbon monoxide, (b) carbon dioxide, (c) methane?
Ans. (a) 42.86 per cent; (b) 27.27 per cent; (c) 75.00 per cent.
171. Calculate the percentage of iron in (a) FeO , (b) Fe_2O_3 , (c) Fe_3O_4 .
Ans. (a) 77.73 per cent; (b) 69.94 per cent; (c) 72.35 per cent.
172. Calculate the percentage composition of $\text{K}_2\text{Cr}_2\text{O}_7$.
Ans. K , 26.59 per cent; Cr , 35.35 per cent; O , 38.06 per cent.
173. Calculate the percentage composition of kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.
Ans. SiO_2 , 46.51 per cent; Al_2O_3 , 39.54 per cent; H_2O , 13.93 per cent.
174. Calculate the percentage composition of dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$.
Ans. Ca , 21.73 per cent; Mg , 13.18 per cent; C , 13.01 per cent; O , 52.08 per cent.
175. Calculate the weight of sodium present in 200 g. of NaHCO_3 .
Ans. 54.76 g.
176. What weight of sulfur is present in 4.730 g. of BaSO_4 ? *Ans.* 0.649 g.
177. What weight of phosphorus can be obtained from 200 lb. of $\text{Ca}_3(\text{PO}_4)_2$?
Ans. 40 lb.
178. What weight of H_2SO_4 can be made from 10 tons of sulfur?
Ans. 30.5 tons.
179. Calculate the number of pounds of pure sulfur necessary to make 2 tons of H_2SO_4 .
Ans. 1,307 lb.
180. A sample of impure silver weighing 0.160 g. is dissolved, and the silver precipitated by adding excess sodium chloride. The silver chloride thus obtained weighs 0.1914 g. Calculate the percentage of silver in the sample.
Ans. 90 per cent.

181. A sample of crude horn silver (impure AgCl) weighing 50 g. contains 15 per cent of impurities. Calculate the weight of silver present in the sample. *Ans.* 31.98 g.
182. A sample of impure silver weighing 10 g. was dissolved in nitric acid, and the resulting solution treated with hydrochloric acid. A precipitate of AgCl weighing 10 g. was obtained. Calculate the percentage purity of the sample of silver. *Ans.* 75.26 per cent.
183. In a laboratory experiment 2.5 g. of Na_2SO_4 was made from 0.563 g. of S. In another experiment 8.82 g. of Na_2SO_4 was made from 2 g. of S. Show that these results illustrate the Law of Definite Proportions. Calculate the theoretical percentage of S in Na_2SO_4 . *Ans.* 22.57 per cent.
184. Calculate the percentage of (a) Al_2O_3 ; (b) water, in common alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. *Ans.* (a) 10.76 per cent; (b) 45.56 per cent.
185. How many pounds of aluminium can be obtained from 10 tons of bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, which contains 65 per cent Al_2O_3 ? *Ans.* 6,894 lb.
186. Assuming that all the lead is available, calculate the amount that can be obtained from 1 ton of pyromorphite, $\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{PO}_4)_2$. *Ans.* 1,527 lb.
187. A sample of copper weighing 10 g. was heated with H_2SO_4 . After the copper had dissolved, water was added. This solution was evaporated to dryness, and 30 g. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was obtained. Calculate the percentage purity of the sample of impure copper. *Ans.* 76.37 per cent.
188. How many pounds of chromite ore containing 57.2 per cent Cr_2O_3 will be required to make 1 ton of pure $\text{K}_2\text{Cr}_2\text{O}_7$? *Ans.* 1,806 lb.
189. How many tons of CaO can be obtained from 10 tons of limestone that contains 95.05 per cent of CaCO_3 ? *Ans.* 5.3 tons.
190. How many pounds of bismuth glance, essentially Bi_2S_3 , containing 72.9 per cent of Bi will be necessary to obtain 500 lb. of anhydrous, C. P. bismuth nitrate, $\text{Bi}(\text{NO}_3)_3$? *Ans.* 362.8 lb.
191. Calculate the weight of insecticide with the composition



that can be made from 10 tons of a lead ore containing 75 per cent of PbS . *Ans.* 27,924 lb.

192. Calculate the number of pounds of disodium hydrogen phosphate, Na_2HPO_4 , that can be made from 1 ton of phosphate rock (impure $\text{Ca}_3(\text{PO}_4)_2$) containing 30.35 per cent P_2O_5 . *Ans.* 1,214 lb.
193. Determine the number of pounds of phosphorus that can be obtained from 1 ton of phosphate rock (impure $\text{Ca}_3(\text{PO}_4)_2$) that analyzes 33.37 per cent P_2O_5 . *Ans.* 293.88 lb.
194. A sample of chromite weighing 1.5195 g. yields 1.5634 g. of lead chromate. Calculate the percentage of Cr_2O_3 in the original sample. *Ans.* 24.21 per cent.
195. A sample of impure sodium chloride weighing 4.00 g. was dissolved in water, and excess silver nitrate added to this solution. The precipitate

- of silver chloride weighed 6.9420 g. Calculate the percentage of chlorine in the original sample. *Ans.* 42.92 per cent.
196. Calculate the weight of potassium in a sample of sylvite, KCl, that contains 2.13 g. of chlorine. *Ans.* 2.35 g.
197. Calculate the weight of copper present in a sample of crystallized copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which, by analysis, contains 53.37 g. of sulfuric anhydride, SO_3 . *Ans.* 42.37 g.
198. How many pounds of phosphorus is required in the manufacture of 1 ton of monoammonium hydrogen phosphate $(\text{NH}_4)\text{H}_2\text{PO}_4$? *Ans.* 539 lb.
199. A sample of impure sodium chloride weighing 2 g. is dissolved in water, and excess silver nitrate added to this solution. The precipitate of silver chloride obtained weighed 4.628 g. Determine the percentage of chlorine in the sample. *Ans.* 57 per cent.
200. A sample of a soluble sulfate weighing 1.023 g. was treated with excess BaCl_2 solution. The precipitate of BaSO_4 obtained weighed 1.509 g. Calculate the percentage of S in the original sample. *Ans.* 20.25 per cent.
201. How many kilograms of phosphorus is necessary to make 100 l. of phosphoric acid having a specific gravity of 1.610 and containing 75 per cent by weight of H_3PO_4 ? *Ans.* 38.2 kg.
202. How many pounds of sulfur is required in the manufacture of 1,000 gal. of sulfuric acid having a specific gravity of 1.835 and containing 93.56 per cent by weight of sulfuric acid? *Ans.* 4,675 lb.
203. How many kilograms of rock salt, 99 per cent NaCl, will be required in the preparation of 20 l. of hydrochloric acid having a specific gravity of 1.2 and containing 39.11 per cent by weight of HCl? *Ans.* 15.2 kg.
204. A sample of brass weighing 2.6235 g. is dissolved in nitric acid, and the lead in the brass is precipitated as PbSO_4 . The precipitate of lead sulfate obtained weighed 0.0147 g. Calculate the percentage of lead in this sample of brass. *Ans.* 0.38 per cent.
205. What weight of superphosphate, $\text{CaH}_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, can be obtained from 100 tons of apatite, essentially $\text{Ca}_5(\text{PO}_4)_3$, which analyzed 30.5 per cent P_2O_5 ? *Ans.* 57.9 tons.
206. Calculate the weight of alum cake, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, that can be obtained from 50 tons of kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, containing 31.25 per cent of Al_2O_3 . *Ans.* 102 tons.

Additional Problems without Answers, for Quizzes

207. What is the molecular weight of each of the following compounds: (a) cane sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$; (b) magnesium ammonium arsenate, $\text{Mg}(\text{NH}_4)\text{AsO}_4$; (c) phosphomolybdic acid, $\text{H}_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 12\text{H}_2\text{O}$; (d) crystallized nickel ammonium sulfate, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$?
208. Determine the molecular weight of each of the following: (a) chloroplatinic acid, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$; (b) potassium fluosilicate, K_2SiF_6 ; (c)

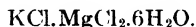
crystallized sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; (d) basic magnesium carbonate, $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$.

209. Find the molecular weights of the following: (a) acid sodium arsenate, $\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$; (b) potassium silver cyanide, $\text{KAg}(\text{CN})_2$; (c) potassium pyrophosphate, $\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$; (d) potassium cobaltinitrite, $2\text{Co}(\text{NO}_2)_3 \cdot 6\text{KNO}_2 \cdot 3\text{H}_2\text{O}$.
210. Calculate the percentage composition of each of the following: (a) lithium carbonate, Li_2CO_3 ; (b) aluminum sodium fluoride (cryolite), $\text{AlF}_3 \cdot 3\text{NaF}$; (c) acid sodium phosphite, $2\text{NaH}_2\text{PO}_3 \cdot 5\text{H}_2\text{O}$.
211. What is the percentage composition of each of the following compounds: (a) lead phosphate, $\text{Pb}_3(\text{PO}_4)_2$; (b) basic nickel carbonate, $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$?
212. Determine the percentage composition of the following: (a) mercuric potassium iodide, $2\text{HgI}_2 \cdot 2\text{KI} \cdot 3\text{H}_2\text{O}$; (b) magnesium hydrogen arsenate, $2\text{MgHASO}_4 \cdot 13\text{H}_2\text{O}$.
213. Calculate the percentage of (a) magnesium in boronite,

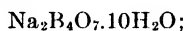


(b) copper in chalcopyrite, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$.

214. Calculate the percentage of (a) KCl , (b) moisture in carnallite,



215. Determine the percentage of (a) boric oxide, B_2O_3 , in borax,



(b) phosphorus pentoxide, P_2O_5 , in magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$.

216. In a laboratory experiment, a student obtained the following data:

5.60 g. of Ag when converted to AgCl yielded 7.45 g. of AgCl .

3.91 g. of Ag when converted to AgCl yielded 5.20 g. of AgCl .

Show how these results illustrate the Law of Definite Proportions.

217. A sample of Epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, weighing 1.2 g. on analysis, yielded 0.585 g. of $\text{Mg}_2\text{P}_2\text{O}_7$. Calculate the percentage of magnesium in the Epsom salts.
218. What weight of sodium could be obtained from 1 ton of sodium chloride that contains 99 per cent NaCl ?
219. How many tons of sulfuric acid can be prepared from 10 tons of pyrites, FeS_2 , containing 42 per cent of sulfur?
220. How much Paris green, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}_3\text{As}_2\text{O}_6$, can be made from the copper obtained from 1 ton of a copper ore that contains 40 per cent CuS ?
221. Calculate the percentage of potassium chloride in a sample of carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, which by analysis contains 35.5 per cent of chlorine.
222. Calculate the percentage of magnesia, MgO , contained in a sample of dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$, that analyzed 40.2 per cent CO_2 .

223. Calculate the percentage purity of a sample of zinc oxide that analyzed 73.6 per cent Zn.
224. Calculate the percentage purity of a sample of silver chloride that contains 18 per cent of chlorine.
225. A sample of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, on analysis gave 30.5 per cent SO_3 . Calculate the percentage purity of the sample.
226. Calculate the percentage purity of a sample of magnesite, MgCO_3 , 1 g. of which was found to contain 0.43 g. of CO_2 .
227. Calculate the percentage purity of a sample of marble, 10 g. of which yielded 1.2 l. of CO_2 at 25°C . and 740 mm. pressure. One liter of CO_2 , at standard conditions, weighs 1.9766 g.
228. Calculate the weight of pyrite, FeS_2 , containing 35.5 per cent of sulfur which gave a precipitate of barium sulfate weighing 1.02 g.
229. A dime (weight 2.488 g.; contains Ag 92.5 per cent, Cu 7.5 per cent) is dissolved in nitric acid. Calculate the weight of AgNO_3 and $\text{Cu(NO}_3)_2$ that can be obtained from the dime.
230. How many pounds of ammonium alum, $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, can be made from 10 tons of alum cake, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$?
231. A sample of chalcopyrite, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$, was found to contain 26.53 per cent of Cu. What weight of chalcopyrite will be required to yield 100,000 lb. of metallic copper?
232. Calculate the tonnage of hematite ore containing 53.5 per cent Fe_2O_3 that will be required to make 100,000 tons of pig iron, 94 per cent Fe.
233. One kilogram of phosphorus, 93 per cent pure, is burned, and the P_2O_5 formed is dissolved in water to produce phosphoric acid. What volume of phosphoric acid solution (sp. gr. 1.43 and containing 60 per cent by weight of H_3PO_4) can be made from the above quantity of phosphorus?

CHAPTER IV

OUTLINE

Dalton observed while determining the composition of methane and ethylene that the different weights of carbon that are united with the same weight of hydrogen are in the proportion of 2:1. Methane and ethylene are very important constituents of natural gas and illuminating gas.

In the oxides of carbon the different weights of carbon that are combined with the same weight of oxygen are in the proportion of 2:1.

In the five oxides of nitrogen the weights of oxygen that are combined with the same weight of nitrogen are in the proportion 1:2:3:4:5.

Dalton thus showed that when two elements combine to form several different compounds, the different weights of the one that are united with a fixed weight of the other are in the proportion of simple whole numbers. This is Dalton's Law of Multiple Proportions.

Dalton's explanation of this law. The Atomic Theory.

THE LAW OF MULTIPLE PROPORTIONS

We have observed that if elements unite to form a certain compound, they always do so in a definite proportion by weight. It has been mentioned, however, that in some cases the same elements can unite in several different proportions to form several different compounds. In these cases, when the proportions in which the elements unite are different, the compounds are different in their properties. For any one of these compounds the proportion in which the elements unite is always the same. We find further that the different weights of the one element that unite with a fixed weight of the second element are in the proportion of simple whole numbers.

Dalton observed this about 1803 while he was analyzing the two gases ethylene and methane. These are different substances with different properties. He found, however, that each of them contained the elements carbon and hydrogen and no others. He found further that the proportions of carbon and hydrogen in the two compounds were different. His results were, of course, not very accurate, for the methods of analysis and the

apparatus that he used at that time were rather crude. The actual proportions of C and H in these compounds are:

	C		H	
	PARTS BY WEIGHT		PARTS BY WEIGHT	
Ethylene.....	24.00	for each	4.032	
Methane.....	12.00	for each	4.032	

The proportion, by weight, of C or of H in either compound is always constant, but it will be observed in the two compounds that the weights of C (24.00 and 12.00) that are combined with the same weight of H (4.032) are different and are in the exact ratio of 2:1.

Having discovered this astounding result for two compounds of carbon and hydrogen, Dalton was led to analyze the compounds of carbon and oxygen. He found that the different weights of oxygen, which in the two compounds were combined with the same weight of carbon were in the ratio of 1:2.

	C		O	
	PARTS BY WEIGHT		PARTS BY WEIGHT	
Carbon monoxide.....	12.00	for each	16.00	
Carbon dioxide.....	12.00	for each	32.00	

The student should show the proportion that exists between the different weights of carbon that are combined with the same weight of oxygen in these two compounds. The answer is that they are in the proportions of 2:1.

Dalton's suspicion that there must be a remarkable principle underlying these simple figures grew into conviction when he again found simple proportions in the oxides of nitrogen. Thus,

	N		O		
	PARTS BY WEIGHT		PARTS BY WEIGHT		
Nitrous oxide.....	28.02	for each	16.00	(1)	
Nitric oxide.....	28.02	for each	32.00	(2)	
Nitrous acid anhydride.....	28.02	for each	48.00	(3)	
Nitrogen peroxide.....	28.02	for each	64.00	(4)	
Nitric acid anhydride.....	28.02	for each	80.00	(5)	

The proportion of nitrogen or of oxygen in any one of the compounds is always constant; but in the five compounds, the different weights of oxygen, combined with the same weight of nitrogen, are in the proportions of 1:2:3:4:5—again simple multiple proportions.

Dalton thus showed that **whenever the same elements unite with each other to form several different compounds,**

the different weights of the one that unite with a fixed weight of the other are in the proportion of small whole numbers. No exceptions to this principle have been found. It is known as Dalton's **Law of Multiple Proportions**. This law has been more amply confirmed by an enormous number of experiments like those originally made by the pioneer Dalton.

Dalton's mind was not satisfied with the deduction of this remarkable principle. He strove for the explanation of it. This was afforded in a brilliant and elegant way by his Atomic Theory of Matter, of which the following quotations give a brief outline:

I. "All bodies of sensible magnitude are constituted of a vast number of extremely small particles or atoms of matter bound together by a force of attraction which as it endeavors to prevent their separation is called attraction or cohesion; but as it collects them from a dispersed state is called attraction of aggregation, or, more simply, affinity."¹

II. "The ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen, etc."²

III. "No new creation or destruction of matter is within the reach of chemical agency. All the elements we can produce consist in separating particles that are in a state of cohesion or combination and joining those that were previously at a distance."³

IV. "The ultimate particles of all simple bodies are atoms, incapable of further division. These atoms (at least viewed along with their atmospheres of heat) are all spheres and are possessed of particular weights which may be denoted by number."⁴

V. "If there are two bodies which are disposed to combine, then their combination takes place by atoms."⁵

VI. "In an elastic gas each particle occupies the center of a comparatively large sphere and supports its dignity by keeping

¹ Dalton's "System of Chemical Philosophy," p. 143.

² Dalton's "New System," p. 141.

³ Dalton's "New System," p. 212.

⁴ Thomson's "History of Chemistry," p. 289.

⁵ Dalton's "New System," p. 216.

all the rest, which by their gravity or otherwise are disposed to encroach upon it, at a respectful distance.”¹

These quaint quotations should be compared with a modern outline of the premises of the Atomic Theory presented in Chap. III.

The Atomic Theory is, however, fully in accord with the great mass of evidence derived from the facts of chemistry and has been extremely useful to scientists. It is, therefore, universally accepted and used.

In the preceding chapter we noted that if we considered the chemical combination of carbon and oxygen as consisting in the union of an individual carbon atom with an individual oxygen atom, we could understand why the elements always unite in the same proportion by weight; *i.e.*, we could understand the constant composition of substances, a matter that finds expression in the Law of Definite Proportions.

If, under certain conditions, a carbon atom can also unite with two oxygen atoms, then the weights that unite will be in the proportion of 12 parts by weight of carbon to 32 parts by weight of oxygen, and this ratio will be definite and unchanged for the combination of any number, say 1 million carbon atoms with 2 million oxygen atoms—12:32. In the other oxide of carbon the weights that unite are in the ratio of 12:16. We note that the weights of oxygen (16 and 32), which combine with the same weight of carbon (12), are in the ratio of 16:32, or 1:2. This is, of course, simply the statement of the Law of Multiple Proportions. It was derived from the concept of atoms uniting.

Let us see how our theory of atoms fits in with some observed facts.

From the evidence of repeated analyses we know that 1 g. of the poisonous oxide of carbon contains 0.4286 g. of carbon and 0.5714 g. of oxygen; *i.e.*,

0.4286 g. of carbon is combined with 0.5714 g. of oxygen.

1 g. of carbon is combined with $1/0.4286 \times 0.5714 = 1.333$ g. of oxygen.

12 g. of carbon is combined with $12 \times 1.333 = 16.00$ g. of oxygen.

¹ Dalton's "System of Chemical Philosophy," p. 143.

Now, 12, the figure used here, is the atomic weight of carbon, and 16 is the atomic weight of oxygen. We find, then, that in the poisonous oxide of carbon the elements are united in the proportion by weight indicating that each atom of carbon is united with one atom of oxygen.

By analysis of the nonpoisonous oxide of carbon we find that 1 g. of this oxide contains 0.2727 g. of carbon and 0.7273 g. of oxygen; *i.e.*,

0.2727 g. of carbon is combined with 0.7273 g. of oxygen.

1 g. of carbon is combined with $1/0.2727 \times 0.7273 = 2.666$ g. of oxygen.

12 g. of carbon is combined with $12 \times 2.666 = 32.00$ g. of oxygen.

That is, in this oxide the elements carbon and oxygen are united in proportion by weight, indicating that each atom of carbon is united with two atoms of oxygen.

The nonpoisonous oxide of carbon contains twice as many oxygen atoms, for each carbon atom, as the poisonous oxide does. We can see then why the weights of oxygen combined with the same weight of carbon are in the proportion of **2:1**.

We have learned from the evidence of repeated analyses that the composition of the oxides of nitrogen can be expressed by the following figures:

	N PARTS BY WEIGHT	O PARTS BY WEIGHT
Nitrous oxide.....	28.02	16.00
Nitric oxide.....	28.02	32.00
Nitrous acid anhydride.....	28.02	48.00
Nitrogen peroxide.....	28.02	64.00
Nitric acid anhydride.....	28.02	80.00

We know that 1 gram-atom of nitrogen (atomic weight of nitrogen) is 14.01 g.

We know that 1 gram-atom of oxygen (atomic weight of oxygen) is 16.00 g.

We can calculate, then, that in the five compounds, the **relative** numbers of atoms of each element in the molecules are

	N NUMBER OF ATOMS	O NUMBER OF ATOMS
Nitrous oxide.....	$\frac{28.02}{14.01} = 2$	$\frac{16.00}{16.00} = 1$
Nitric oxide.....	$\frac{28.02}{14.01} = 2$	$\frac{32.00}{16.00} = 2$
Nitrous acid anhydride.....	$\frac{28.02}{14.01} = 2$	$\frac{48.00}{16.00} = 3$
Nitrogen peroxide.....	$\frac{28.02}{14.01} = 2$	$\frac{64.00}{16.00} = 4$
Nitric acid anhydride.....	$\frac{28.02}{14.01} = 2$	$\frac{80.00}{16.00} = 5$

For two nitrogen atoms, in each case, the number of oxygen atoms present is, respectively, 1, 2, 3, 4, and 5 in the five different compounds. We can see, then, why the weights of oxygen combined with the same weight of nitrogen are in the proportion of 1:2:3:4:5.

The concepts of the Atomic Theory applied to the results of analysis thus explain the Laws of Definite and Multiple Proportions.

Example 1.—The two chlorides of iron have the following composition:

Ferrous chloride...	Fe = 44.05 per cent	Cl = 55.95 per cent
Ferric chloride....	Fe = 34.42 per cent	Cl = 65.58 per cent

Show how these illustrate the Law of Multiple Proportions.

By expressing the composition of the substances in percent, the evidence of Multiple Proportions is hidden; but it can easily be brought out by calculating the amount of chlorine in each case combined with 1 part by weight of iron. Thus, in ferrous chloride, 44.05 g. of iron is combined with 55.95 g. of chlorine.

1 g. of iron is combined with $1/44.05 \times 55.95 = 1.270$ g. of chlorine.

In ferric chloride 34.42 g. of iron is combined with 65.58 g. of chlorine.

1 g. of iron is combined with $1/34.42 \times 65.58 = 1.905$ g. of chlorine.

The weights of chlorine that are united with the same weight of iron (1 g. of iron) are in the proportion of 1.270:1.905, and these are in the ratio of **2:3**, for $1.270/2 = 0.635$, and $1.905/3 = 0.635$.

Example 2.—Three oxyacids of sulfur have the following composition:

Sulfurous acid.....	{	H = 2.456 per cent
	{	S = 39.061 per cent
	{	O = 58.482 per cent
Sulfuric acid.....	{	H = 2.055 per cent
	{	S = 32.688 per cent
	{	O = 65.255 per cent
Pyrosulfuric acid.....	{	H = 1.131 per cent
	{	S = 35.994 per cent
	{	O = 62.874 per cent

SULFUROUS ACID

2.456 g. of H is combined with 39.061 g. of S and with 58.482 g. of O.

1 g. of H is combined with $1/2.456 \times 39.061 = 15.904$ g. of S.

1 g. of H is combined with $1/2.456 \times 58.482 = 23.811$ g. of O.

SULFURIC ACID

2.055 g. of H is combined with 32.688 g. of S and with 65.255 g. of O.

1 g. of H is combined with $1/2.055 \times 32.688 = 15.906$ g. of S.

1 g. of H is combined with $1/2.055 \times 65.255 = 31.754$ g. of O.

PYROSULFURIC ACID

1.131 g. of H is combined with 35.994 g. of S and with 62.874 g. of O.

1 g. of H is combined with $1/1.131 \times 35.994 = 31.824$ g. of S.

1 g. of H is combined with $1/1.131 \times 62.874 = 55.591$ g. of O.

The weights of sulfur that are combined with the same weight of hydrogen (1 g.) in the three compounds are 15.90 g., 15.90 g., 31.824 g. These are in the proportion **1:1:2**.

The weights of oxygen combined with 1 g. of hydrogen, in the three compounds, are, respectively, 23.81 g., 31.754 g., 55.591 g. These are in the proportion **3:4:7**; for

$$\frac{23.81}{3} = 7.94 \quad \frac{31.754}{4} = 7.94 \quad \frac{55.591}{7} = 7.94$$

If we know the molecular formula of any one of the three oxyacids of sulfur, we can write the molecular formulas of the

others. Thus, if we know that the molecular formula of sulfurous acid is H_2SO_3 , then that of sulfuric acid must be H_2SO_4 , and of pyrosulfuric acid $\text{H}_2\text{S}_2\text{O}_7$, for the oxygen in the three compounds is in the ratio **3:4:7** for the same amount of hydrogen. The sulfur is the same in the first two and twice as great in the third.

Problems

234. The three oxides of phosphorus have the following compositions:

(a) P = 56.395 per cent	O = 43.604 per cent
(b) P = 49.238 per cent	O = 50.761 per cent
(c) P = 43.693 per cent	O = 56.306 per cent

The molecular weights of the respective oxides are (a) 110.08, (b) 126.08, (c) 142.08. Show that these compounds illustrate the Law of Multiple Proportions.

235. Tin forms two oxides that have the following composition:

(a) Sn = 88.121 per cent	O = 11.878 per cent
(b) Sn = 78.765 per cent	O = 21.234 per cent

Show that these compounds illustrate the Law of Multiple Proportions.

236. Three oxyacids of chlorine have the following composition:

(a) H = 1.902 per cent	Cl = 67.584 per cent	O = 30.514 per cent
(b) H = 1.192 per cent	Cl = 41.984 per cent	O = 56.824 per cent
(c) H = 1.003 per cent	Cl = 35.294 per cent	O = 63.703 per cent

Show that these illustrate the Law of Multiple Proportions.

237. Hydrogen and oxygen form two compounds of the following composition:

(a) H = 11.190 per cent	O = 88.819 per cent
(b) H = 5.926 per cent	O = 94.073 per cent

Show that these illustrate the Law of Multiple Proportions. (a) is water. Give the name and formula of (b).

238. Potassium, chlorine, and oxygen form four compounds that have the following percentage composition:

(a) K = 43.176 per cent	Cl = 39.156 per cent	O = 17.667 per cent
(b) K = 36.692 per cent	Cl = 33.277 per cent	O = 30.030 per cent
(c) K = 31.902 per cent	Cl = 28.932 per cent	O = 39.164 per cent
(d) K = 28.220 per cent	Cl = 25.591 per cent	O = 46.188 per cent

Show that these illustrate the Law of Multiple Proportions.

- 239.** Sodium, sulfur, and oxygen form three compounds of the following composition:

(a) Na = 36.490 per cent	S = 25.432 per cent	O = 38.077 per cent
(b) Na = 32.380 per cent	S = 22.567 per cent	O = 45.051 per cent
(c) Na = 29.091 per cent	S = 40.551 per cent	O = 30.356 per cent

Show that these illustrate the Law of Multiple Proportions.

- 240.** Three potassium salts have the following composition:

(a) K = 49.412 per cent	S = 20.257 per cent	O = 30.331 per cent
(b) K = 44.876 per cent	S = 18.398 per cent	O = 36.726 per cent
(c) K = 30.748 per cent	S = 25.212 per cent	O = 44.040 per cent

Show that these illustrate the Law of Multiple Proportions.

- 241.** Three oxyacids of nitrogen have the following percentage composition:

(a) H = 3.250 per cent	N = 45.149 per cent	O = 51.599 per cent
(b) H = 2.144 per cent	N = 29.782 per cent	O = 68.073 per cent
(c) H = 1.599 per cent	N = 22.219 per cent	O = 76.181 per cent

Show that these illustrate the Law of Multiple Proportions.

- 242.** Two oxides of antimony have the following composition:

(a) Sb = 83.356 per cent	O = 16.634 per cent
(b) Sb = 75.031 per cent	O = 24.968 per cent

Show that these illustrate the Law of Multiple Proportions.

- 243.** Two oxides of arsenic have the following composition:

(a) As = 75.747 per cent	O = 24.252 per cent
(b) As = 65.205 per cent	O = 34.794 per cent

Show that these compounds illustrate the Law of Multiple Proportions.

- 244.** K, Cr, and O form two compounds of the following composition:

(a) K = 40.26 per cent	Cr = 26.77 per cent	O = 32.95 per cent
(b) K = 26.59 per cent	Cr = 35.39 per cent	O = 38.02 per cent

Show that these illustrate the Law of Multiple Proportions.

- 245.** Show by calculations that the following compounds conform to and illustrate the Law of Multiple Proportions.

(a) K_2O = 48.50 per cent	CrO_3 = 51.50 per cent
(b) K_2O = 32.02 per cent	CrO_3 = 67.98 per cent

- 246.** In one chloride of copper it is found that 31.5 g. of copper is combined with 17.57 g. of chlorine. In another different chloride of copper, it is found that 40.38 g. of copper is combined with 45.05 g. of chlorine. Show by calculations that these compounds conform to and illustrate the Law of Multiple Proportions.

- 247.** In the various oxides of lead, it is found that the weights of lead and of oxygen that enter into chemical combination are as follows:

In plumbic oxide 59.412 g. of Pb is combined with 4.588 g. of O.

In lead sesquioxide 179.24 g. of Pb is combined with 20.76 g. of O.

In lead oxide 129.93 g. of Pb is combined with 20.07 g. of O.

Show by calculations that these compounds conform to and illustrate the Law of Multiple Proportions.

- 248.** Nitrogen and oxygen combine to form five different oxides, and it is found that nitrous oxide contains 21.015 g. of N combined with 12 g. of O.

Nitric oxide contains 21.23 g. of N combined with 24.27 g. of O.

Nitrogen sesquioxide contains 8.3631 g. of N combined with 14.3369 g. of O.

Nitrogen dioxide contains 6.1478 g. of N combined with 14.0522 g. of O.

Nitrogen pentoxide contains 4.0185 g. of N combined with 11.4815 g. of O.

Show by calculations that these compounds conform to and illustrate the Law of Multiple Proportions.

- 249.** Manganese and oxygen form several oxides. It is found that

50 g. of manganous oxide contains 38.721 g. of Mn combined with 11.279 g. of O.

60 g. of manganese sesquioxide contains 41.756 g. of Mn combined with 18.244 g. of O.

70 g. of manganese dioxide contains 44.232 g. of Mn combined with 25.768 g. of O.

80 g. of manganese trioxide contains 42.693 g. of Mn combined with 37.307 g. of O.

90 g. of manganese heptoxide contains 44.566 g. of Mn combined with 45.434 g. of O.

Show by calculations that the foregoing oxides of manganese conform to and illustrate the Law of Multiple Proportions.

- 250.** It is found that in mercurous chloride 1 g. of Hg is combined with 0.1767 g. of Cl and in mercuric chloride 1 g. of Cl is combined with 2.8285 g. of Hg. Show that these two compounds illustrate the Law of Multiple Proportions.
- 251.** In phosphorus trichloride it is found that 1 g. of P is combined with 3.427 g. of Cl, and in phosphorus pentachloride 1 g. of Cl is combined with 0.17507 g. of P. Show by calculations that these two chlorides of phosphorus illustrate the Law of Multiple Proportions.
- 252.** Iron forms two oxides of the following composition:

(a) Ferrous oxide—Fe = 77.73 per cent O = 22.27 per cent

(b) Ferric oxide—Fe = 69.94 per cent O = 30.06 per cent

Show by calculations that these values are in accordance with the Law of Multiple Proportions.

- 253.** Na, H, P, and O form two compounds of the following composition:

- (a) Na = 32.383 per cent H = 0.7069 per cent P = 21.851 per cent
 O = 45.056 per cent
 (b) Na = 32.155 per cent H = 1.409 per cent P = 21.697 per cent
 O = 44.737 per cent

Show that these illustrate the Law of Multiple Proportions.

- 254.** Two sulfates of sodium have the following composition:

- (a) Na_2O = 43.643 per cent SO_3 = 56.356 per cent
 (b) Na_2O = 27.912 per cent SO_3 = 72.087 per cent

Show that these illustrate the Law of Multiple Proportions.

- 255.** H_2O and P_2O_5 form acids of the following composition:

- (a) H_2O = 11.253 per cent P_2O_5 = 88.747 per cent
 (b) H_2O = 27.557 per cent P_2O_5 = 72.443 per cent

Show that these illustrate the Law of Multiple Proportions.

- 256.** Two sulfates of iron have the following composition:

- (a) Fe = 36.761 per cent S = 21.106 per cent O = 42.132 per cent
 (b) Fe = 27.929 per cent S = 24.053 per cent O = 48.016 per cent

Show that these illustrate the Law of Multiple Proportions.

- 257.** When strongly heated, 2.5 g. of potassium chlorate lost 0.98 g. of oxygen. Similarly, 4.16 g. of potassium perchlorate lost 1.918 g. of oxygen. Show by calculations that these figures illustrate the Law of Multiple Proportions.

- 258.** Three compounds of hydrogen, carbon, and chlorine have the following composition by weight:

- (a) C = 23.779 per cent H = 5.989 per cent Cl = 70.232 per cent
 (b) C = 14.135 per cent H = 2.374 per cent Cl = 83.481 per cent
 (c) C = 10.066 per cent H = 0.844 per cent Cl = 89.110 per cent

Show that these compounds conform to and illustrate the Law of Multiple Proportions.

- 259.** Three compounds of hydrogen, carbon, and bromine have the following composition by weight:

- (a) C = 12.758 per cent H = 3.214 per cent Br = 84.028 per cent
 (b) C = 22.035 per cent H = 4.625 per cent Br = 73.340 per cent
 (c) C = 12.780 per cent H = 2.146 per cent Br = 85.074 per cent

Show that these compounds conform to the Law of Multiple Proportions.

- 260.** Four compounds of hydrogen and carbon have the following composition:

- (a) C = 85.620 per cent H = 14.380 per cent
- (b) C = 92.252 per cent H = 7.748 per cent
- (c) C = 79.878 per cent H = 20.122 per cent
- (d) C = 74.858 per cent H = 25.142 per cent

Show that these compounds conform to the Law of Multiple Proportions.

- 261.** Methyl alcohol (a) and ethyl alcohol (b) have the following compositions by weight:

- (a) C = 37.472 per cent H = 12.585 per cent O = 49.943 per cent
- (b) C = 52.130 per cent H = 13.132 per cent O = 34.738 per cent

Show that ethyl alcohol and methyl alcohol conform to and illustrate the Law of Multiple Proportions.

- 262.** Formic acid (a) and acetic acid (b), two common organic acids, have the following composition:

- (a) C = 26.086 per cent O = 69.533 per cent H = 4.381 per cent
- (b) C = 39.984 per cent O = 53.290 per cent H = 6.726 per cent

Show that these two acids conform to the Law of Multiple Proportions.

- 263.** Sodium tetraborate forms two hydrates. One of these contains 47.233 per cent water of crystallization, and the other contains 30.919 per cent water of crystallization.

Show by means of calculations that these hydrates conform to the Law of Multiple Proportions.

- 264.** Metaboric acid (a), orthoboric acid (b), and tetraboric acid (c) have the following compositions:

- (a) H = 2.300 per cent B = 24.790 per cent O = 72.910 per cent
- (b) H = 4.890 per cent B = 17.496 per cent O = 77.614 per cent
- (c) H = 1.281 per cent B = 27.515 per cent O = 71.204 per cent

Show that the three boric acids conform to the Law of Multiple Proportions.

- 265.** Five compounds of hydrogen, oxygen, and nitrogen have percentage compositions as follows:

- (a) N = 27.441 per cent H = 9.873 per cent O = 62.686 per cent
- (b) N = 28.569 per cent H = 6.168 per cent O = 65.263 per cent
- (c) N = 45.149 per cent H = 3.250 per cent O = 51.599 per cent
- (d) N = 29.782 per cent H = 2.144 per cent O = 68.073 per cent
- (e) N = 22.219 per cent H = 1.599 per cent O = 76.181 per cent

Show that these illustrate the Law of Multiple Proportions.

- 266.** Three compounds of the following composition are known. Show that the Law of Multiple Proportions is illustrated.

(a) N = 82.247 per cent H = 17.753 per cent

(b) N = 87.420 per cent H = 12.580 per cent

(c) N = 97.658 per cent H = 2.342 per cent

- 267.** Three compounds of iron and sulfur have the following compositions:

(a) Fe = 46.557 per cent S = 53.443 per cent

(b) Fe = 63.527 per cent S = 36.473 per cent

(c) Fe = 53.728 per cent S = 46.272 per cent

Show that these illustrate the Law of Multiple Proportions.

- 268.** Two compounds of calcium, carbon, and oxygen have the following compositions:

(a) Ca = 31.285 per cent C = 18.746 per cent O = 49.969 per cent

(b) Ca = 40.041 per cent C = 11.996 per cent O = 47.963 per cent

Show that these illustrate the Law of Multiple Proportions.

- 269.** Two compounds of calcium, carbon, and nitrogen are known and have the following compositions:

(a) Ca = 43.509 per cent C = 26.071 per cent N = 30.420 per cent

(b) Ca = 50.031 per cent C = 14.988 per cent N = 34.981 per cent

Show that these illustrate the Law of Multiple Proportions.

- 270.** Nitroglycerin (a) and trinitrotoluene (b) have the following compositions:

(a) C = 18.462 per cent H = 2.584 per cent N = 21.542 per cent

(b) C = 37.006 per cent H = 2.219 per cent N = 18.505 per cent

(a) O = 57.412 per cent

(b) O = 42.270 per cent

Show that these conform to and illustrate the Law of Multiple Proportions.

- 271.** Isoprene (a) and benzene (b) have the following percentage compositions:

(a) C = 88.158 per cent H = 11.842 per cent

(b) C = 92.252 per cent H = 7.748 per cent

• Show that these conform to and illustrate the Law of Multiple Proportions.

- 272.** Three common solvents, acetone (a), ether (b), and ethyl alcohol (c), have the following compositions:

(a) C = 62.029 per cent H = 10.416 per cent O = 27.555 per cent

(b) C = 64.803 per cent H = 13.603 per cent O = 21.594 per cent

(c) C = 52.130 per cent H = 13.132 per cent O = 34.738 per cent

Show that these conform to and illustrate the Law of Multiple Proportions.

- 273.** Copper sulfate forms three hydrates containing, respectively, 10.141, 25.294, and 36.073 per cent of water of hydration.

Show that these hydrates conform to the Law of Multiple Proportions.

- 274.** By means of a physical chemical study it can be shown that ferric chloride forms four hydrates containing the following percentages of water of hydration: (a) 57.134, (b) 43.742, (c) 35.705, and (d) 30.760.

Show that these hydrates conform to the Law of Multiple Proportions.

- 275.** It can be shown that calcium nitrate forms four hydrates containing the following percentages of water of hydration: (a) 9.895, (b) 17.915, (c) 24.774, (d) 30.516.

Show that these hydrates conform to and illustrate the Law of Multiple Proportions.

CHAPTER V

OUTLINE

Gay-Lussac found by experiment that, when gases combine, the volumes that unite are in the proportion of simple whole numbers. The volume of any product that is a gas is related to the volumes of the gases that reacted, in the proportion of simple whole numbers. This is Gay-Lussac's Law of Volumes.

Avogadro's Law. Equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules.

Avogadro's Law explains Gay-Lussac's Law of Volumes.

Proof that the molecules of each of the gases hydrogen, and chlorine contain two atoms and should hence be written, respectively, H_2 , and Cl_2 .

The volume occupied at standard conditions by **1 gram-molecular weight** (1 gram-mol) (g.-mol) of a substance in the gaseous state is approximately **22.4 l.** This holds true for a great many substances. This volume is called the **gram-molecular volume**, or **molar volume**.

Molecular-weight determinations by vapor-density, boiling-point, and freezing-point methods.

GAY-LUSSAC'S LAW OF VOLUMES; AVOGADRO'S LAW

RELATION BETWEEN VOLUME AND MOLECULAR WEIGHT

We have observed that when elements unite, they do so in *definite* proportions by weight, and in some cases we have seen that the same elements unite in several proportions. The different weights of the one element that unite with the same weight of the other are in the proportion of small whole numbers. We have seen how, from an enormous number of careful observations, the Laws of Definite and Multiple Proportions were deduced. We have further seen that the Atomic Theory affords a simple and beautiful explanation of these two laws (and that the laws, in turn, serve to strengthen the statements of the Atomic Theory).

When the elements that unite are gases, we find that the action is governed by a further simple law. The **volumes** of the gases that unite are in the proportion of small whole numbers.

If the product formed is a gas, its volume will be related, by a simple proportion, to the volumes of the gases that united.

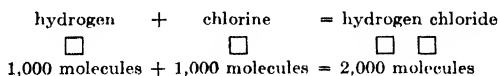
This was first observed by Gay-Lussac and Humboldt in 1805. They found, when hydrogen and oxygen united to form water, that 2 parts by volume of hydrogen united with exactly 1 part by volume of oxygen. If more hydrogen or more oxygen was used than required by the proportion 2:1, the excess of hydrogen or oxygen remained uncombined.

Gay-Lussac further proved that when hydrogen and chlorine unite, 1 part by volume of hydrogen unites with exactly 1 part by volume of chlorine and forms exactly 2 parts by volume of hydrogen chloride. When ammonia and hydrogen chloride unite, 1 part by volume of ammonia unites with 1 part by volume of hydrogen chloride and forms 1 part by volume of ammonium chloride vapor. He further showed that 2 parts by volume of ammonia were formed from the union of 1 part by volume of nitrogen and 3 parts by volume of hydrogen. In all the cases that he observed, the volumes of gases that united were in simple proportion. One part by volume of a gas united with 1 part by volume of another, or 1 part by volume of a gas with 2 parts by volume of another, or 1 with 3, or 2 with 1, or 2 with 2, or 2 with 3, etc. He did not find any case where, for example, 1 part by volume of a gas united with a complex proportion such as 2.177 parts by volume of another. Gay-Lussac, therefore, concluded that "gases always unite in the simplest proportions by volume." This conclusion of Gay-Lussac's has been amply confirmed by a large number of experiments since then, and we now state it as a law. **Gay-Lussac's Law of Volumes: When gases unite with one another, the volumes that unite are in the proportion of simple whole numbers. If the product is a gas, its volume is related to the volumes of the gases that reacted, in the proportion of simple whole numbers.** These simple volume proportions recall the way in which the atoms unite.

Gay-Lussac suspected that the explanation of the law he had discovered would be afforded by Dalton's Atomic Theory. He was, however, unable to work out this explanation, although he came close to it. We shall see that the keynote of the explanation was given by Avogadro (in 1811), who made the assumption that

equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. This hypothesis is now generally accepted as a true generalization. It is now known as the **Law of Avogadro**.

By applying Gay-Lussac's Law of Volumes and Avogadro's Law, it is possible to determine the number of atoms present in a molecule of each of the elementary gases, hydrogen, oxygen, nitrogen, and chlorine. For example: It is an experimental fact that 1 volume of hydrogen unites with 1 volume of chlorine and forms 2 volumes of hydrogen chloride (Gay-Lussac's Law). According to Avogadro's Law, these equal volumes of gases contain the same numbers of molecules. For convenience, assume that we choose a volume of gas occupied by 1,000 molecules; then



Each of the 2,000 molecules of hydrogen chloride must contain at least 1 atom of hydrogen and at least 1 atom of chlorine. We cannot have a half or other fraction of an atom. Therefore, in 2,000 molecules of hydrogen chloride there are at least 2,000 atoms of hydrogen. But we had 1,000 molecules of hydrogen before combination with chlorine took place. That is, 2,000 atoms of hydrogen must be derived from 1,000 molecules of hydrogen, or 2 atoms of hydrogen from each molecule of hydrogen. So 1 molecule of hydrogen must contain at least 2 atoms of hydrogen and is represented by the molecular formula H_2 . Similar reasoning applies to show that the chlorine molecule contains 2 atoms of chlorine, or Cl_2 . Proofs like this one presented will justify the conclusion that the elementary gases oxygen and nitrogen are diatomic molecules and have the molecular formulas O_2 and N_2 , respectively. In the case of the inert gases He, Ne, Ar, Kr, and Xe the molecules are monatomic, and the symbols of these elements represent the molecular formulas of these elements.

GRAM-MOLECULAR VOLUME, OR MOLAR VOLUME

We have learned that 1 gram-atom of oxygen is equal to 16.00 g. of oxygen; and since there are two atoms in a molecule of oxygen,

1 gram-mol of oxygen, O_2 , contains 2×16.00 g., or 32.00 g. of oxygen, or there are 32.00 g. of oxygen in 1 gram-mol of oxygen.

The density of oxygen is 1.429 g. per liter at S.T.P., or,

1.429 g. of oxygen occupies 1 l. at S.T.P.

1 g. of oxygen occupies $1/1.429$ l., or 0.7 l., at S.T.P.

32.00 g., or 1 gram-mol, of oxygen, O_2 , will occupy 32.00×0.7 l., or 22.40 l. at S.T.P.

Similarly, 1 gram-mol of nitrogen, N_2 , contains 28.02 g.

The density or the weight of 1 l. of nitrogen at S.T.P. is 1.2505 g.

28.02 g., or 1 gram-mol, of nitrogen, N_2 , will occupy

$28.02/1.2502$ l., or 22.4 l. at S.T.P.

Also, 1 gram-mol of ammonia, NH_3 , contains 17.034 g. of ammonia.

The weight of 1 l. of ammonia at S.T.P. is 0.7621 g.

17.034 g., or 1 gram-mol, of ammonia, NH_3 , will occupy $17.034/0.7621$ l., or 22.35 l. at S.T.P.

Thus, if we divide the weight of 1 gram-mol of any gas at S.T.P. by the weight of 1 l. of that gas at S.T.P. (density), a value approximately 22.4 l. is obtained for each gas. We have, thereby, deduced one of the most useful principles in chemical calculations: that **1 gram-mol of any gas occupies 22.4 l. at standard conditions** (S.T.P.), and this volume is generally referred to as the **gram-molecular volume**, or simply the **molar volume**.

Since there are deviations from the gas laws, such as that caused by the attraction of the molecules of a gas for one another; the molar volume will in some cases become slightly less than 22.4 l. The slight error involved in using the number 22.4 in such cases is negligible for most calculations where the principle is useful.

From the foregoing it becomes obvious that, if one knows the weight of 1 l. of a gas at S.T.P. (density), simply multiplying this density $\times 22.4$ gives the molecular weight of the gas. Or, if the molecular weight of a gas is known, to find its density at S.T.P. it is necessary only to divide the molecular weight of the gas by 22.4.

It is well to recall the statement made in Chap. III regarding the chemical formula that it not only represents a gram-mol of the substance but also represents a gram-molecular volume or molar volume of a gas at S.T.P. Thus, the formula for carbon dioxide, CO_2 , represents not only 44 g., or 1 gram-mol, of carbon dioxide (S.T.P.) but also 22.4 l. (S.T.P.), the molar volume of carbon dioxide. This relationship enables the student to make direct conversions from weight to volumes, and vice versa, when dealing with gases. The principle will be used over and over again in the chapters that follow. Of utmost importance is it to the student that he thoroughly master the significance of the molar volume.

It is of special interest to note that the number of grams in 1 oz. avoirdupois is 28.35 and that the number of liters in 1 cu. ft. is 28.31. This approximate coincidence makes possible the use of the metric system and the U. S. A. system of weights and measures interchangeably when dealing with gases. It follows that 1 ounce-mol of any gas occupies 22.4 cu. ft. at S.T.P. The student will find this a very convenient conversion in dealing with chemical reactions of gases.

It frequently becomes necessary, especially in industrial chemical calculations and in metallurgical calculations, to deal with larger volumes of gases; and under these circumstances the molecular weight of the gas is expressed in kilograms (kg.), and the volume that it occupies is expressed in cubic meters (cu. m.). Thus, 1 kilogram-mol of any gas occupies 22.4 cu. m. at S.T.P. Likewise, 1 pound-mol of any gas occupies 16×22.4 , or 358.4 cu. ft., at S.T.P.

All this information leads us to further extensions of "what a chemical formula stands for." In summarizing, we can definitely state that as far as molecular weight and volume ratios of gases are concerned, the formula, for example, of carbon dioxide, CO_2 , can represent the following relationships:

- (a) 44 g., or 1 gram-mol, of carbon dioxide occupies 22.4 l. at S.T.P. (molar volume).
- Or (b) 44 kg., or 1 kilogram-mol, of carbon dioxide occupies 22.4 cu.m. at S.T.P.
- Or (c) 44 oz., or 1 ounce-mol, of carbon dioxide occupies 22.4 cu.ft. at S.T.P.

Or (d) 44 lb., or 1 pound-mol, of carbon dioxide occupies 358.4 cu.ft. at S.T.P.

To be sure, this summary would apply to any other gas, and its importance in chemical calculations cannot be overemphasized.

The following examples will serve to illustrate the application of Gay-Lussac's Law and Avogadro's Law.

Example 1.—Determine the weight in kilograms of 100 cu. m. of hydrogen sulfide at S.T.P.

1 kilogram-mol of H_2S occupies 22.4 cu. m. at S.T.P.

100 cu. m. of H_2S will be equivalent to $100/22.4$, or 4.46 kilogram-mols, of H_2S at S.T.P.

Since 1 kilogram-mol of H_2S contains 34.06 kg. of H_2S ,

4.46 kilogram-mols of H_2S will contain 4.46×34.06 , or 151.91 kg., of H_2S at S.T.P.

Example 2.—What volume in cubic feet will 10 lb. of hydrogen sulfide gas occupy at S.T.P.?

There are 34.06 lb. of H_2S contained in 1 pound-mol of H_2S .

10.0 lb. of H_2S will be contained in $10.0/34.06 = 0.294$ lb.-mol of H_2S .

Now, 1 pound-mol of H_2S occupies 358.4 cu. ft. at S.T.P.

0.294 pound-mol of H_2S will occupy 0.294×358.4 cu. ft. =
105.37 cu. ft. at S.T.P.

The gram-molecular weight of a gas may be obtained from its vapor density by applying the Avogadro Law.

The vapor density of nitrogen is 13.91. This means that 1 l. of nitrogen is 13.91 times as heavy as 1 l. of hydrogen, both gases under the same conditions of temperature and pressure.

A liter of nitrogen contains the same number of molecules as a liter of hydrogen, both gases being under the same conditions of temperature and pressure (Law of Avogadro). Therefore,

1 molecule of nitrogen is 13.91 times as heavy as 1 molecule of hydrogen. Or,

1 gram-mol of nitrogen is 13.91 times as heavy as 1 gram-mol of hydrogen.

1 gram-mol of hydrogen is 2.016 g.; then

1 gram-mol, or one gram-molecular weight, of nitrogen will be 13.91×2.016 g. = 28.04 g.

Generally, if M = one gram-molecular weight (1 gram-mol) of a gas

$$M = \text{vapor density} \times 2.016$$

THE DETERMINATION OF THE MOLECULAR WEIGHT OF VOLATILE LIQUIDS

The molecular weight of liquid substances that can be vaporized without decomposition is obtained by the Victor Meyer method. This method assumes the molecular weight of the

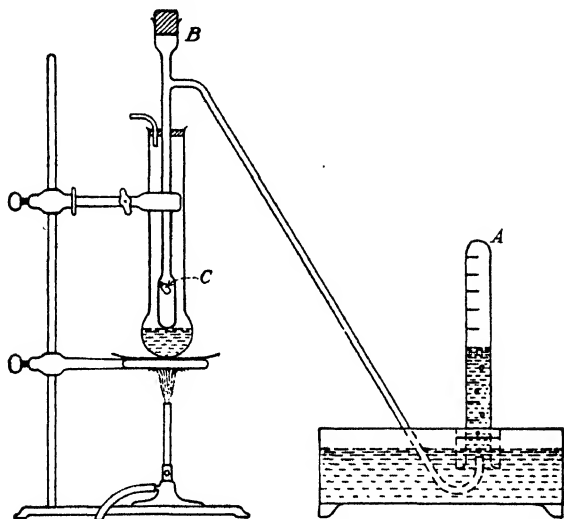


FIG. 10.—Victor Meyer method for molecular-weight determinations of volatile liquids.

substance in the liquid phase to be the same as that in the vapor phase. The essential details of the method are as follows: A weighed amount of the liquid substance contained in the small ampoule C (Fig. 10) is vaporized in the jacketed tube filled with air. The vapor displaces a volume of air equal to its own volume. This air, in turn, displaces its own volume of water in the eudiometer A , which corresponds to the volume of the vapor of the liquid substance whose molecular weight is to be determined. The volume of air displaced is noted by observing the water displaced. Also, the temperature and barometric pressure are recorded. Then corrections are made for the difference in levels

of the water inside the eudiometer and in the trough, as well as for vapor pressure of water at the temperature of the experiment. This is followed by reducing the measured volume of air to standard conditions of temperature and pressure and by the calculation of the weight of 22.4 l. of the vapor, which equals the molecular weight of the liquid substance.

Many solids and liquids require such high temperatures for their vaporization that it is impractical to determine their molecular weight by the vapor-density method. In some cases, also, the solid or liquid decomposes at temperatures required to vaporize it. It is fortunate that we have other methods for the determination of molecular weights. Two closely related are the so-called boiling-point and freezing-point methods which depend on the effect of a solute in raising the boiling point or of lowering the freezing point of a solvent.

MOLECULAR-WEIGHT DETERMINATION BY BOILING-POINT AND FREEZING-POINT METHODS

Molecules of liquid are constantly escaping from the surface of a liquid, as indicated by Fig. 11. As the liquid is heated, the

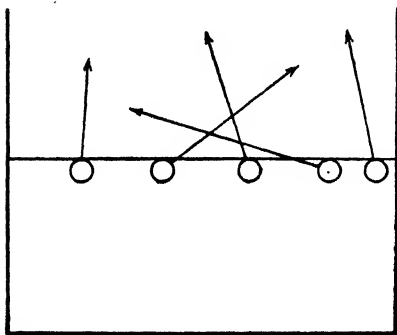


Fig. 11.

kinetic energy of the molecules increases steadily, and consequently the number escaping per second from each square centimeter of surface is increased. We often think of this in terms of the statement *The vapor pressure of a liquid increases with rise of temperature.* When, however, some relatively nonvolatile substance is dissolved in a sol-

vent, thus making a solution, the number of molecules of solvent escaping per second from each square centimeter of surface will be decreased. This is due partly to the fact that there are always some molecules of the dissolved substance at the surface and that therefore the solvent molecules are hindered from getting to the surface in a purely mechanical way. Also, the process of solution is not a matter of filling voids in the liquid. When a

substance dissolves in a liquid, it is an indication of an attractive force between the molecules of solvent and solute, and in most cases the attractive force of solute molecules for solvent molecules is greater than that of solvent molecules for each other. The solute molecules, therefore, hold back the solvent molecules near them by a force of molecular attraction. The number of solvent molecules escaping per second is reduced. The vapor pressure of the liquid at any temperature is thus decreased; and consequently in order to attain a vapor pressure of, say, one atmosphere, the solution (solvent and solute) must be heated to a higher temperature than that required for the solvent alone. The boiling point of a solution is always higher than that of the pure solvent if the solute is nonvolatile.

The greater the number of solute molecules for a given number of solvent molecules the greater the effect and the greater the difference between the boiling point of the pure solvent and that of the solution. This difference is usually spoken of as the rise in boiling point and is often represented by the symbol ΔT .

Similarly, the crystallization or freezing of a solvent is interfered with by the presence of foreign molecules, and this effect is also proportional to the number of these molecules present in a given weight of solvent. It is therefore necessary to cool a solution below the freezing point of the pure solvent in all cases before freezing will begin.

The difference in temperature is spoken of as the depression of the freezing point and is represented by the symbol ΔT .

The number of individual molecules in 1 mol of a substance is 6.06×10^{23} . You will realize at once that it is impracticable to base our study on individual single molecules; but if we deal in each case with **one gram-molecular weight** (1 gram-mol) of various substances, we are comparing equal numbers of individual molecules, and we know exactly how many such molecules are present.

Exact experiment has established the correctness of the picture painted for individual molecules, and thus it has been found that

1 gram-mol (342 g.) of cane sugar, $C_{12}H_{22}O_{11}$, dissolved in 1 l. of water raises the boiling point $0.52^{\circ}C$.

1 gram-mol (46 g.) of ethyl alcohol, C_2H_5OH , dissolved in 1 l. of water raises the boiling point $0.52^\circ C$.

1 gram-mol (92 g.) of glycerin, $C_3H_8O_3$, dissolved in 1 l. of water raises the boiling point $0.52^\circ C$.

One-tenth gram-mol of cane sugar in 1 l. of H_2O raises the boiling point $\frac{1}{10} \times 0.52^\circ$; other quantities of a wide range of materials act accordingly. The rise in boiling point obtained is, therefore, proportional to the number of individual molecules of the dissolved substance (solute).

If a given quantity of solute, say 1 gram-mol, is dissolved in 10 l. of water instead of 1 l., the effect of the solute molecules should be reduced to one-tenth; or, to express accurately the effect of the solvent, we say that the rise is inversely proportional to the number of solvent molecules, or to the weight of volume of the solvent.

The boiling-point rise ΔT is \propto to the weight w of the solute, or to the number of gram-mols of solute w/M , where M is the molecular weight of the solute.

The boiling-point rise ΔT is inversely \propto to the weight W of solvent or to the number of gram-mols W/M_1 of solvent, where M_1 is the molecular weight of the solvent. M_1 is, of course, known.

If one number (ΔT) is proportional to another, it equals some constant K_1 times the other.

$$\Delta T = \frac{K_1 \frac{w}{M}}{\frac{W}{M_1}}$$

Transposing

$$M = \frac{K_1 M_1 w}{\Delta T W}$$

Since M_1 is a known number, it can be combined with the number K_1 , or $K_1 M_1 = K$. Then in 1,000 g. of solvent

$$M = 1,000 \frac{K w}{\Delta T W}$$

We know w and W and can determine ΔT . We can, therefore, calculate M , the molecular weight of the solute, if K is known for the solvent used.

The value of K , the proportionality factor, or constant, can be determined by dissolving a measured weight of a substance whose molecular weight is known, in a known weight or volume of the solvent to be used. Then, in the foregoing relationship, every factor is known except K , and we can solve for K . Considering benzol as a solvent in the determination of the molecular weight of a material, say an oil, we dissolve 0.2 g. of a known material such as anthracene, $C_{14}H_{10}$ (molecular weight = 178), in 25 g. of benzol and find that the boiling point of the solution is 0.120° higher than that of pure benzol.

$$M = 1,000 \frac{Kw}{\Delta T W} \quad K = \frac{M \Delta T W}{1,000 w} = \frac{178 \times 0.120 \times 25}{1,000 \times 0.2}$$

$$K = 2.670$$

Values of K for various solvents are given in physical chemistry books and in books of chemical tables. A few values for some frequently used solvents are given in Table IX. The constants are given for both the boiling-point and the freezing-point methods.

TABLE IX

Substance	K for boiling-point method	K for freezing-point method
Chloroform.....	3.41	
Ethyl alcohol.....	1.14	
Benzine.....	2.67 ✓	5.12
Ether.....	2.01	
Acetone.....	1.67	
Water.....	0.512	1.855
Phenol.....	7.4

A convenient apparatus, frequently used to determine the molecular weights of solids and liquids, is shown in Fig. 12. This consists of a glass test tube with a side arm connected to a condenser. A weighed quantity of solvent is introduced into the tube which is tightly closed by a cork. A special sensitive thermometer, called a Beckmann thermometer in recognition of its inventor, projects through the cork with its bulb fully

immersed in the liquid. Beckmann thermometers are graduated to read in thousandths of one degree. The long scale covers only 5° . By means of an ingenious overflow arrangement, the quantity of mercury can be changed, thus permitting the thermometer to be adjusted or set to cover any desired 5° range. Thus, the same thermometer can be used for a temperature range from 0°C. to 5°C. , or from 95°C. to 100°C. , by simply transferring mercury from a reservoir to the bulb or from

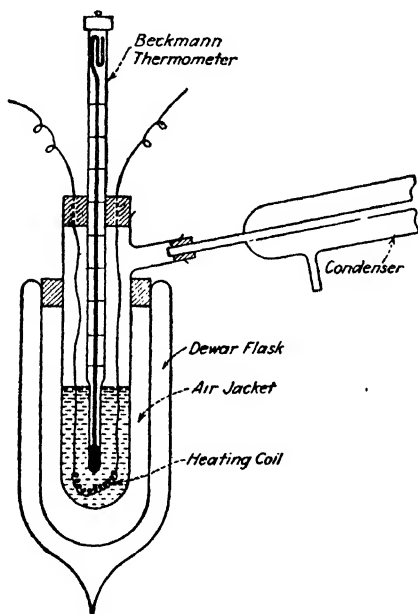


FIG. 12.—Boiling-point apparatus.

the bulb to the reservoir. This simple invention made it practicable to have thermometer readings to $\frac{1}{1000}^{\circ}$ or even $\frac{1}{10000}^{\circ}$; and this, in turn, made it possible to measure boiling-point elevations or freezing-point depressions with sufficient accuracy to determine the molecular weight of substances by this principle.

A heating element in the liquid causes the liquid to boil evenly and steadily so as to prevent undue fluctuations while reading the thermometer in obtaining the boiling point of the solvent or of the solution. The water condenser causes the vapor from the

boiling liquid to condense and returns it to the tube. A small percentage of the solvent is thus always either in the form of vapor or running back from the condenser into the tube. The weight of solvent in the tube at any instant is therefore a little less than the quantity weighed out. This quantity can be determined and subtracted as a correction to give a more accurate result.

After the boiling point of the pure solvent has been determined, a weighed quantity of the solute is introduced, and a little time allowed for it to dissolve if it is a solid and to become uniformly distributed and for the temperature of the whole apparatus to reach equilibrium at the slightly higher value. When several successive values are nearly constant, the temperature is again taken and recorded. The difference in the two temperatures, *i.e.*, that of solvent alone and solvent plus solute, is the boiling-point rise ΔT .

In like fashion the molecular weight of a solute may be determined by measuring the depression of the freezing point of a solvent caused by the introduction of a weighed quantity of the solute. The apparatus (Fig. 13) differs from the boiling-point apparatus in that, instead of being heated by a burner, the tube is cooled by immersion in a large vessel containing a liquid which is several degrees colder than the freezing point of the solvent. Benzol freezes at 5.4°C . If it is used as a solvent, the tube is immersed in ice water maintained at a temperature of 1°C . to 2°C . Again, a jacket around the inner tube is used to minimize temperature fluctuations and to avoid breakage. In general, temperature fluctuations from any cause are to be carefully avoided. No side arms or condensers are needed for the freezing-point method, but in this case the liquid in both inner

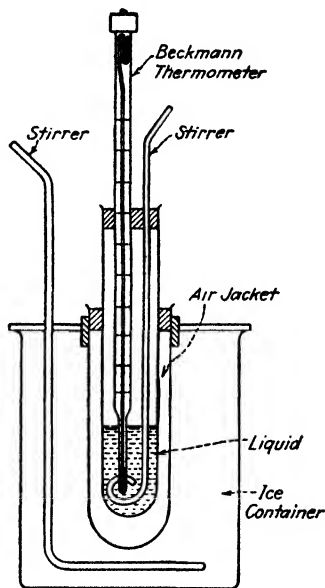


FIG. 13.—Freezing-point apparatus.

jacket and outside bath must be stirred, preferably at a uniform rate, in order to prevent temperature inequalities.

When the temperature has dropped to the point where freezing begins, the latent heat of fusion is given, and the temperature rises above the true freezing point and then falls again. On account of this, many liquids supercool before freezing begins. It is, therefore, highly advisable that a definite technique be developed by repeated trials and that factors such as rate of cooling and extent of supercooling be kept constant. In this way duplicable results can be obtained.

Choice of which method to use depends on the nature of the substance whose molecular weight is to be found, the boiling and freezing points of the solvent selected, and other features not appropriate here. If a substance has an appreciable vapor pressure or tendency to decompose at the boiling point of the solvent to be used, the freezing-point method would naturally be used. The relationship of solute and solvent in the freezing-point method must be such that the first crystals to separate out on cooling are pure solvent, not solute or a solid solution of the two.

Acids, bases, and salts, or electrolytes, in general, ionize in solution to various degrees and thus give rise to larger numbers of individual particles than would be assumed from the weight of material used. Electrolytes therefore give "abnormal" boiling-point elevations and abnormal freezing-point depressions. These abnormal values can be used to calculate not the molecular weight of the electrolyte but its degree of ionization, if the molecular weight is known.

Further details are given in laboratory manuals on physical chemistry.

Problems

- 276.** Express (a) 224 cu. ft. of nitrogen (S.T.P.) and (b) 220 lb. of carbon dioxide (S.T.P.) in terms of the pound-mol.

Ans. (a) 0.625 lb.-mol; (b) 50 pound-mol.

- 277.** Express (a) 100 lb. of nitrogen (S.T.P.) and (b) 672 cu. ft. of oxygen (S.T.P.) in terms of the pound-mol.

Ans. (a) 3.57 lb.-mol; (b) 1.875 pound-mol.

- 278.** Express (a) 33.6 cu.m. of carbon dioxide (S.T.P.) and 10 kg. of chlorine (S.T.P.) in terms of the kilogram-mol.

Ans. (a) 1.5 kg.-mol; (b) 0.1408 kilogram-mol.

279. Express (a) 12 kg. of argon (S.T.P.) and 100 cu. m. of helium (S.T.P.) in terms of the kg.-mol.
Ans. (a) 0.030 kg.-mol; (b) 4.46 kilogram-mol.
280. Determine (a) the volume of 10 lb. of chlorine at S.T.P.; (b) the volume of 0.15 pound-mol of nitrogen at S.T.P.
Ans. (a) 5.04 cu. ft.; (b) 53.76 cu. ft.
281. Calculate the "hypothetical, or average, molecular weight" of air if 450 cc. of air weighs 0.5818 g. under standard conditions.
Ans. 28.96.
282. What volume will 8 g. of oxygen occupy at 21°C. and 705 mm. pressure?
Ans. 6.478 l.
283. The molecular weight of a gas is 26.016. Calculate the weight of 1 l. of the gas at 24°C. and 742 mm. pressure.
Ans. 1.042 g.
284. The molecular weight of argon is 39.9. What is the weight of 1 l. of the gas at 21°C. and 745 mm. pressure?
Ans. 1.621 g.
285. Nitrous oxide has a molecular weight of 44. Calculate the weight of 150 cc. of the gas under standard conditions.
Ans. 0.2946 g.
286. Calculate the molecular weight of that substance 10 g. of which in the gaseous state occupies 10 l. at 10°C. and 1,000 mm. pressure.
Ans. 17.65.
287. A sample of a volatile liquid weighing 0.08 g., when vaporized, yielded 32 cc. of vapor at 27°C. and 740 mm. pressure. Calculate the molecular weight of the substance.
Ans. 63.33.
288. Calculate the molecular weight of a gas 0.091 g. of which occupies 33.5 cc. at 100°C. and 740 mm. pressure.
Ans. 85.39.
289. It was found that 1.225 g. of a gas occupies 1.1 l. when measured over water at 22°C. and 743 mm. Calculate the molecular weight of the gas. Vapor pressure of water at 22°C. = 19.7 mm.
Ans. 28.34.
290. Calculate the weight of hydrogen contained in a gas holder of 5 l. capacity under a pressure of 35 mm. and a temperature of 22°C.
Ans. 0.0191 g.
291. A gas has a vapor density of 18.05. What is the weight of 5,182 cc. of this gas measured at 21°C. and 752 mm. pressure?
Ans. 7.674 g.
292. At what temperature will 4 g. of oxygen, measured under standard conditions, occupy a volume of 5.6 l., the pressure remaining the same?
Ans. 273°C.
293. Calculate the weight in ounces of hydrogen sulfide in a gasometer of 1.5 cu. ft. capacity under a pressure of 762 mm. and a temperature of 22°C.
Ans. 2.11 oz.
294. What weight of carbon dioxide in ounces will be contained in a gas holder of 2 cu. ft. capacity under a pressure of 15.6 lb. per sq. in. and at a temperature of 21°C.?
Ans. 3.87 oz.
295. What weight of oxygen will occupy the same volume as 0.504 g. of hydrogen, both gases at standard conditions?
Ans. 8 g.

- 296.** It was found that 120 cc. of water vapor, measured at 180°C. and 740 mm. pressure, weighed 0.0566 g. Show from these data that the molecular weight of water vapor is 18.016.
- 297.** A quantity of helium weighing 8 g., at standard conditions, is forced into a flask of 6-l. capacity, temperature remaining constant. Calculate the pressure in the flask. *Ans.* 7.4 atm.
- 298.** The relative density of chlorine referred to air is 2.4491. Calculate the molecular weight of chlorine. *Ans.* 70.92.
- 299.** A sample of a volatile liquid weighing 0.1 g. when vaporized in a Victor Meyer apparatus displaced 20 cc. of air. The temperature of the air was 17°C., and the barometer reading was 710 mm. Calculate the molecular weight of the liquid. Vapor pressure of water at 17°C. = 14.5 mm. *Ans.* 130.0.
- 300.** A volatile liquid, weighing 0.125 g., when vaporized, yielded 31 cc. of vapor, measured over mercury at 100°C. and 735 mm. barometric pressure. The level of the mercury in the measuring tube was 200 mm. above the level of the mercury in the trough. Calculate (a) the vapor density of the substance, (b) the molecular weight of the liquid.
Ans. (a) 87.5; (b) 175.
- 301.** Calculate the molecular weight of an organic compound from the following data:
- | | |
|-------------------------------|------------|
| Weight of compound taken..... | 0.4618 g. |
| Volume of vapor obtained..... | 265.36 cc. |
| Temperature..... | 75.0°C. |
| Barometer reading..... | 640.3 mm. |
- Ans.* 58.72.
- 302.** Calculate the molecular weight of oxygen from the following data:
A test tube containing a mixture of potassium chlorate and manganese dioxide was heated, and the oxygen driven off displaced 377.4 cc. of water. The temperature was 21°C., and the barometric pressure 747.4 mm. At the end of the experiment the test tube was found to have lost 0.4798 g. *Ans.* 31.70.
- 303.** A volume of gas measuring 2.825 l., collected over water at 23°C. and 755 mm. pressure, is found to weigh 3.1275 g. when deprived of water vapor. Determine the molecular weight of the gas. Vapor pressure of water at 23°C. = 20.9 mm. *Ans.* 26.95.
- 304.** Determine the molecular weight of chloroform, using the Victor Meyer method, from the following data:
- | | |
|----------------------------------------|-----------|
| Weight of sample taken..... | 2.016 g. |
| Volume of air displaced..... | 440.0 cc. |
| Temperature..... | 16.5°C. |
| Barometer reading..... | 707.5 mm. |
| Vapor pressure of water at 16.5°C..... | 14.0 mm. |
- Ans.* 119.28.
- 305.** In a laboratory experiment a student found that a tube containing KClO_3 lost 0.5 g. on heating. The oxygen evolved measured 375 cc.

- at 28°C. when collected over water under barometric pressure of 749 mm. Calculate the weight of 1 l. of oxygen at standard conditions. Vapor pressure of water at 28°C. = 28.1 mm. *Ans.* 1.55 g.
306. Calculate the molecular weight of a certain gas, 1.13 l. of which, collected over water at 24°C. and 754 mm. pressure, weighed 1.251 g. when deprived of the aqueous vapor. Vapor pressure of water at 24°C. = 22.2 mm. *Ans.* 28.02.
307. A certain metal weighing 0.3288 g. when treated with excess acid displaced 0.472 l. of hydrogen, collected over water at 22°C. and 750 mm. pressure. Calculate the weight of this metal that displaces 2.016 g. of hydrogen at standard conditions. Vapor pressure of water at 22°C. = 19.7 mm. *Ans.* 17.58 g.
308. It was found that 30 g. of an organic compound dissolved in 500 cc. of water gave a boiling point of 100.173°C. What is the molecular weight of the substance? *Ans.* 180.3.
309. What weight of glucose, $C_6H_{12}O_6$, dissolved in 500 cc. of water is necessary to give a freezing-point lowering of 0.15°C.? *Ans.* 7.26 g.
310. It was determined that 0.365 g. of a substance dissolved in 90 g. of benzene gave a freezing-point depression of 0.45°C. Calculate the molecular weight of the substance. *Ans.* 45.0.
311. The boiling point of acetone is elevated 0.105°C. by 0.090 g. of a substance when dissolved in 10 g. of acetone. Calculate the molecular weight of the substance. *Ans.* 143.0.
312. Calculate the weight of ethyl alcohol, C_2H_5OH , when dissolved in 200 cc. of water that will give a freezing-point depression of 0.12°C. *Ans.* 0.594 g.

Additional Problems without Answers, for Quizzes

313. A volume of a gas measuring 220 cc. weighs 0.6445 g. at 0°C. and 760 mm. pressure. Calculate (a) the vapor density of the gas, (b) its relative density referred to air, (c) its relative density referred to oxygen.
314. The density of a gas is 1.2507 g./l. at S.T.P. Calculate the molecular weight of the gas.
315. The weight of 100 cc. of methane, under standard conditions, is 0.0714 g. Calculate the molecular weight of this substance.
316. A substance has a molecular weight of 4.0. Calculate the weight of 440 cc. of the substance in gaseous form at standard conditions.
317. Calculate the weight of 200 cc. of hydrogen sulfide at 18°C. and 740 mm. pressure.
318. The relative density of a certain gas referred to air is 0.6908. Calculate the molecular weight of the gas.
319. The relative density of carbon dioxide referred to oxygen is 1.3831. Calculate the molecular weight of CO_2 .
320. The relative density of hydrogen sulfide referred to air is 1.177. Calculate (a) the density of the gas in grams per liter at S.T.P., (b) vapor density of the gas, (c) the molecular weight of hydrogen sulfide.

- 321.** A quantity of gas weighing 2.5 g. with a density of 1.25 g./l. at S.T.P. is collected over water at 20°C. and 750 mm. pressure. Calculate the volume occupied by the gas under these conditions. Vapor pressure of water at 20°C. = 17.4 mm.
- 322.** Calculate the volume occupied by 0.2016 g. of hydrogen when measured in a container over water at 24°C. and 755.5 mm. pressure. Vapor pressure of water at 24°C. = 22.2 mm.
- 323.** A quantity of acetylene, weighing 0.5 g. (density = 1.161 g./l. at S.T.P.), is collected over water at 25°C. and 758 mm. pressure. What volume does the gas occupy? Vapor pressure of water at 25°C. = 23.5 mm.
- 324.** Fourteen grams of nitrogen was mixed with 35.46 g. of chlorine. Both gases measured at standard conditions. Calculate (a) the volume occupied by the mixture, (b) the density of the mixture in grams per liter at S.T.P., (c) the relative density of the mixture referred to air.
- 325.** Calculate (a) the vapor density, (b) the molecular weight of an organic compound from the following data:

Weight of compound taken.....	0.150 g.
Volume of vapor obtained.....	30.500 cc.
Temperature.....	95.0°C.
Barometer reading.....	745.0 mm.

Mercury in the eudiometer 345 mm. above the level of the Hg in the trough.

- 326.** Calculate the molecular weight of benzene vapor from the following data:

Weight of benzene taken.....	0.3625 g.
Volume of vapor obtained.....	143.75 cc.
Temperature.....	100.0°C.
Barometer reading.....	752.0 mm.

- 327.** Calculate the weight of 1 mol of carbon tetrachloride from the following data obtained by the Victor Meyer method:

Weight of compound taken.....	0.8680 g.
Volume of air displaced.....	135.66 cc.
Temperature.....	21.0°C.
Barometer reading.....	750.0 mm.
Vapor pressure of water at 21.0°C.....	18.5 mm.

- 328.** In a molecular-weight determination by the Victor Meyer method, 240 mg. of a volatile substance displaced 40 cc. of air, measured at 27°C. and 765 mm. pressure. What is the weight of 1 gram-mol of the compound? Vapor pressure of water at 27°C. = 26.5 mm.
- 329.** A glass bulb of 250 cc. capacity is filled with vapor which weighs 625 mg., measured at 273°C. and 1 atm. pressure. Calculate the weight of 2 gram-mols of the vapor.

- 330.** Determine the weight of a sample of chloroform, CHCl_3 , that will be necessary to displace 25 cc. of air, measured at a temperature of 22°C . and a barometer reading of 750 mm., using a Victor Meyer apparatus. Vapor pressure of water at 22°C . = 19.7 mm.
- 331.** What weight of carbon tetrachloride, CCl_4 , will be required to displace 22.4 cc. of air, measured at 21°C . and 1 atm. pressure, using a Victor Meyer apparatus? Vapor pressure of water at 21°C . = 18.5 mm.
- 332.** If the molecular weight of a gas is 26, determine the volume of air, measured at 25°C . and 740 mm. pressure, that will be displaced in a Victor Meyer apparatus by 58 mg. of the gas. Vapor pressure of water at 25°C . = 23.5 mm.
- 333.** The molecular weight of an organic compound is 78.048. Calculate the volume of vapor, measured at 100°C . and 750 mm. pressure, that will be obtained from 100 mg. of the substance.
- 334.** Calculate the volume of vapor, measured at 75°C . and 755 mm. pressure, that can be obtained from 200 mg. of acetone, 1 gram-mol of which weighs 58.05 g.
- 335.** Calculate the weight in kilograms of 200 cu. m. of hydrogen sulfide, at a temperature of 25°C . and 750 mm. pressure.
- 336.** Calculate the weight in kilograms of 32 cu. m. of oxygen, at a temperature of 20°C . and 740 mm. pressure.
- 337.** What volume will 100 kg. of carbon dioxide occupy, at 22°C . and 760 mm. pressure?
- 338.** Calculate the volume 10 kg. of nitrogen will occupy, measured at 27°C . and 745 mm. pressure.
- 339.** Calculate the weight in tons of helium required to fill a dirigible of 6,500,000-cu. ft. capacity, at a temperature of 22°C . and a pressure of 760 mm.
- 340.** Calculate the weight of 1 l. of oxygen at S.T.P. from the following data:
- | | |
|-----------------------------------------------------------------------|----------------------|
| Weight of tube + KClO_3 + MnO_2 before heating..... | 21.786 g. |
| Weight of tube + residue after heating..... | 20.546 g. |
| Volume of oxygen collected over water..... | 956 cc. |
| Temperature..... | 23°C . |
| Barometric pressure..... | 761 mm. |
| Vapor pressure of water at 23°C | 20.9 mm. |
- 341.** Determine (a) the volume of 2 pound-mols of ammonia at S.T.P.; (b) the volume of 2 lb. of ammonia at S.T.P.
- 342.** Calculate the volume occupied by 25 lb. of ammonia at 70°F . and 14.7 lb. per sq. in.
- 343.** Calculate the volume occupied by 10 lb. of carbon dioxide at 72°F . and 750 mm. Hg pressure.
- 344.** Calculate the weight of 1,000 cu. ft. of chlorine measured at 32°F . and 755 mm. Hg pressure.
- 345.** Calculate the volume of 1 kilogram-mol of ammonia at 21°C . and 758 mm. of Hg pressure.

CHAPTER VI

OUTLINE

Chemical formulas are derived from the results of analysis.

Chemical formulas represent weights.

The weight of an element present, divided by the relative weight of an atom of that element, gives the relative number of atoms of that element present.

The **empirical formula** represents the **relative** number of atoms of each element in one molecule of the compound.

The **molecular formula** represents the **actual** number of atoms of each element in one molecule of the compound.

To determine the molecular formula it is necessary to know the molecular weight of the compound or to be able to determine the molecular weight of it.

Formulas of minerals.

DERIVATION OF CHEMICAL FORMULAS

In the preceding chapters we have stressed the importance and the significance of the chemical formula. Particularly have we emphasized the fact that it represents the composition of a chemical compound. The composition of a given material is obtained usually by, first, a qualitative chemical analysis, followed by a quantitative analysis of it. The qualitative analysis gives information as to the nature of the various constituents present in the unknown material. The quantitative analysis establishes the proportion by weight of the elements in the compound, and this is usually expressed as the percentage composition of these constituents. Before proceeding to illustrate the method of determining the chemical formula of a substance, it is well to make the following statements: (a) that formula which represents the relative numbers of atoms present (weight relations only) is called an **empirical formula**; (b) that formula which represents not only the relative numbers of atoms in one molecule but also the actual number of atoms of each element in the molecule of the compound is known as the **molecular formula**. In order to establish the true molecular formula of a compound, it is necessary to know not only the percentage

composition by weight but also the molecular weight of that substance or have sufficient data at hand to enable one to determine the molecular weight by various methods described in Chap. V. However, these methods apply only to gases, liquids, and solids that are readily vaporized (volatile). In the case of solids that are nonvolatile (high melting point), there is no direct method available by which the molecular weight of the substance can be determined. It is possible to obtain knowledge concerning the molecular weight of crystalline substances whose ultimate crystal structure is known from information obtainable by X-ray crystal analysis. This is beyond the scope of this text. In dealing with nonvolatile solids, then, the empirical formula is considered to be the molecular formula for a particular solid. We shall see how this applies in deriving the formulas for that very interesting realm of crystalline solids occurring in nature, *viz.*, the minerals.

Let us consider three types of problems in deriving the molecular formula of a substance dealing with (a) a gas; (b) volatile liquid; (c) nonvolatile solids.

Example 1.—The percentage composition of a gaseous hydrocarbon is 85.62 per cent carbon and 14.38 per cent hydrogen. The weight of 1 l. of the gas is 1.2609 g. at S.T.P. Determine the molecular formula of the hydrocarbon.

The percentage composition of the compound is

$$\text{C} = 85.62 \text{ per cent} \quad \text{H} = 14.38 \text{ per cent}$$

This, of course, means that 100 g. of the hydrocarbon contains 85.62 g. of C and 14.38 g. of H.

Since 1 gram-atom of C = 12.00 g. and 1 gram-atom of H = 1.008 g., there will be

$$\frac{85.62}{12.00} \quad 7.135 \text{ gram-atoms of C}$$

and

$$\frac{14.38}{1.008} = 14.265 \text{ gram-atoms of H in this hydrocarbon}$$

For each 7.135 gram-atoms of C there are 14.265 gram-atoms of H. Then for each 1 gram-atom of C there will be $14.265/7.135$

= 2 gram-atoms of H, or the ratio of 1 gram-atom of C to 2 gram-atoms of H, or C:H = 1:2.

The empirical formula for the hydrocarbon, then, is CH_2 .

The weight of 1 l. of the gas is 1.2609 g. at S.T.P.

Since 1 gram-mol is the weight of 22.4 l. of the gas at S.T.P. (molar volume), then $22.4 \times 1.2609 \text{ g.} = 28.244 \text{ g.}$ which corresponds to 1 gram-mol of the hydrocarbon at S.T.P., or its molecular weight.

The empirical formula CH_2 represents 1 gram-mol as containing 12.00 g. of C + 2.016 g. of H, or 14.016 g. However, the calculated weight of 1 gram-mol of the hydrocarbon gave 28.244 g. This is just twice the weight represented by the empirical formula. Therefore, the molecular formula must be C_2H_4 , since this represents a molecular weight of 28.032. This is the chemical formula of the well-known gas ethylene. The slight discrepancy between the calculated molecular weight and that represented by the molecular formula may be attributed to slight errors in the analysis and also in the density determination. However, the calculated molecular weight is sufficiently accurate to establish the molecular formula as C_2H_4 and not any other multiple of CH_2 .

Example 2.—The chemical analysis of a volatile liquid organic compound gave the following percentage composition:

C = 40.00 per cent H = 6.70 per cent O = 53.30 per cent

It was found that 300 mg. of the liquid yielded 166.7 cc. of vapor at 130°C. and 755 mm. of Hg. From this information establish the true molecular formula of the compound.

From the analysis:

100 g. of the compound contains 40.00 g. of C, 6.70 g. of H, and 53.30 g. of O. Then

$$\frac{40.00}{12.00} = 3.33 \text{ gram-atoms of C}$$

$$\frac{6.70}{1.008} = 6.65 \text{ gram-atoms of H}$$

$$\frac{53.30}{16.00} = 3.33 \text{ gram-atoms of O}$$

It is obvious that the weight ratios of $C:H:O = 3.33:6.65:3.33 = 1:2:1$. The empirical formula of the compound will be CH_2O . To establish the true molecular formula of this substance, as previously stated, requires knowledge of the molecular weight. The determination of the molecular weight is the next step in our solution. We have the information that

Three hundred milligrams, or 0.3 g., of the compound yielded 166.7 cc. of vapor at $130^\circ C$. and 755 mm. of Hg. It is necessary to reduce this volume to standard conditions of temperature and pressure. Then

$$\frac{V}{166.7 \text{ cc.}} \times \frac{T}{273/403} \times \frac{P}{755/760} = 112 \text{ cc. at S.T.P.}$$

112 cc. or 0.112 l. (S.T.P.) of vapor weighs 0.3 g.

Since 1 gram-mol of any gas occupies 22.4 l. at S.T.P., then

22.4 l. of the vapor weighs $22.4 \times 0.3/0.112 \text{ g.} = 60.0 \text{ g.} = 1 \text{ gram-mol}$, or the molecular weight of the compound.

The empirical formula CH_2O represents 1 gram-mol as containing 30.016 g., but the data above show that 1 gram-mol of the compound contains 60.0 g. This is approximately twice the weight represented by the empirical formula. Therefore the true molecular formula of the compound must be $C_2H_4O_2$. This formula happens to represent the formula for one of the common organic acids, acetic acid, usually written $HC_2H_3O_2$. The organic chemist would represent it as CH_3COOH .

It should be noted here that molecular formulas of liquid substances that can be vaporized without decomposition, as in the foregoing example, are obtainable by assuming the molecular weight of the substance in the liquid phase to be the same as that in the vapor phase. The Victor Meyer method, described and illustrated in Chap. V, is useful in the determination of the molecular weight of these types of substances. Molecular-weight determinations of substances that cannot be vaporized without decomposition but can be dissolved in some solvent are made by the freezing-point or the boiling-point method.

FORMULAS OF MINERALS ARE EMPIRICAL FORMULAS

A mineral may be defined as any chemical element or compound occurring in nature and usually possessing a definite

crystalline structure. The elements sulfur, carbon (in the form of diamond and graphite), copper, gold, and silver found in the earth's crust are examples of simple element minerals. The various silicate, carbonate, and sulfate rocks are typical examples of the more complex type of inorganic minerals. Anthracite and bituminous coal and asphalt would be natural occurring organic minerals. The silicate minerals are of considerable interest to almost everyone. They are widely distributed over the earth and, to be sure, are crystallographically complicated and of complex chemical composition. Great credit is due to W. H. Bragg and W. L. Bragg, who have pioneered in the field of X-ray analysis of silicate minerals, for their classification into a very few groups of all the silicates whose crystal structures are known. A chemical analysis of a mineral will give some idea of the constituents present in it. It does not give information as to how the atoms are combined or arranged in the structure. It is the purpose in this text to concern ourselves with a few examples of how chemical formulas may be assigned to minerals from the percentage composition of the mineral. Since the molecular weights of minerals cannot be determined directly, the formula established for its composition will of necessity be the empirical one.

The following example is a mineral made up of a chemical combination of elements.

Example 1.—The chemical analysis of a specimen of arsenopyrite, or mispickel, from Czecho-Slovakia by Palmer (U. S. Geol. Survey *Bull.* 878, p. 84) gave the following results:

Fe = 34.30 per cent, As = 45.51 per cent, S = 19.75 per cent

From this analysis 100 g. of the mineral contains

$$\begin{array}{rcl} \frac{34.30}{55.84} & = & 0.614 \text{ gram-atom of Fe} \\ \frac{45.51}{74.91} & = & 0.608 \text{ gram-atom of As} \\ \frac{19.75}{32.06} & = & 0.613 \text{ gram-atom of S} \end{array}$$

The weight ratios of the various atoms in this mineral, then, Fe:As:S = 0.614:0.608:0.613, are in the nearest whole-number

ratio of 1:1:1. Therefore, the empirical formula of arsenopyrite is FeAsS and is sometimes written as $\text{FeS}_2 \cdot \text{FeAs}_2$.

The slight discrepancy in the foregoing ratios is due, undoubtedly, to small amounts of impurities in the mineral and also to the fact that the percentage composition from chemical analysis is only a close approximation to the true composition. We are justified, therefore, in reducing the weight ratios to the nearest whole numbers to establish the chemical formula of the mineral.

The chemical composition of a great many minerals, of greater complexity than the preceding example, is indicated by expressing the various elements combined with oxygen in terms of percentages of various oxides present. As an example of this type of mineral, let us consider the widely distributed material known as kaolinite, a hydrated aluminum silicate. It is used in large quantities in the manufacture of ceramic materials such as chinaware, porcelain, tiles, insulators, and refractory products.

Example 2.—The chemical analysis of kaolinite, the composition of which is expressed in terms of the various oxides, is

Silica, SiO_2	= 46.06 per cent
Alumina, Al_2O_3	= 39.63 per cent
Water, H_2O	= 14.31 per cent

What is its empirical formula?

In representing the formula of the mineral, we express the weight ratios in terms of the ratios of gram-mols of the oxides present. Thus,

1 gram-mol of SiO_2	= 60.06 g. of SiO_2
1 gram-mol of Al_2O_3	= 101.94 g. of Al_2O_3
1 gram-mol of H_2O	= 18.016 g. of H_2O

From the analysis, 100 g. of kaolinite contains

$\frac{46.06}{60.06}$	= 0.767 gram-mol of SiO_2
$\frac{39.63}{101.94}$	= 0.388 gram-mol of Al_2O_3
$\frac{14.31}{18.016}$	= 0.794 gram-mol of H_2O

The weight ratios of the various oxides follow:

$\text{SiO}_2:\text{Al}_2\text{O}_3:\text{H}_2\text{O} \approx 0.767:0.388:0.794$. These numbers are in the nearest whole-number ratios of 2:1:2. The empirical formula of kaolinite would be written $2\text{SiO}_2.\text{Al}_2\text{O}_3.2\text{H}_2\text{O}$ or, more correctly, $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$.

When a mineral contains small amounts of other oxides that are similar in chemical nature to the several oxides present in major amounts, these small amounts are regarded as impurities. It is assumed that these oxides have replaced chemically equivalent amounts of the principal oxides. The relative numbers of molecules of these are added in with the number of molecules of the oxides that they probably replaced, thus giving the relative numbers of molecules of the major oxides before replacement took place. This procedure removes unnecessary complications of the formula of the mineral and, at the same time, compensates for the effect of the small amounts of oxides which are regarded as impurities.

Example 3.—Derive the empirical formula of the mineral albite (a feldspar) which has the following composition:

Silica, SiO_2	= 68.22
Alumina, Al_2O_3	= 19.06
Ferric oxide, Fe_2O_3	= 0.15
Lime, CaO	= 0.40
Soda, Na_2O	= 11.47
Potassa, K_2O	= 0.20

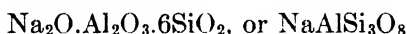
The weight ratios in terms of gram-mols of the various oxides are as follows:

$$\begin{aligned} \frac{68.22}{60.06} &= 1.136 \text{ gram-mols of } \text{SiO}_2 \\ \frac{19.06}{101.94} &= 0.1869 \text{ gram-mol of } \text{Al}_2\text{O}_3 \\ \frac{0.15}{159.68} &= 0.0009 \text{ gram-mol of } \text{Fe}_2\text{O}_3 \\ \frac{0.4}{56.08} &= 0.0071 \text{ gram-mol of } \text{CaO} \\ \frac{11.47}{61.994} &= 0.1850 \text{ gram-mol of } \text{Na}_2\text{O} \\ \frac{0.2}{94.2} &= 0.0021 \text{ gram-mol of } \text{K}_2\text{O} \end{aligned}$$

The 0.0009 gram-mol of Fe_2O_3 may be regarded as having replaced an equal number of gram-mols of Al_2O_3 . Likewise, the 0.0071 gram-mol of CaO and 0.0021 gram-mol of K_2O may be regarded as having replaced an equal number of gram-mols of Na_2O . The small numbers of gram-mols of the minor ingredients Fe_2O_3 , CaO , and K_2O are therefore added to the number of gram-mols of the respective oxides that they are regarded as having replaced. The total numbers of gram-mols thus obtained are used in deriving the formula of the mineral. This is conveniently assembled in the following tabular form:

Oxide	Per cent	Molecular weight	Relative number of gram-mols		
SiO_2	68.22	60.06	1.136	1.136	6
Al_2O_3	19.06	101.94	0.1869	1
Fe_2O_3	0.15	159.68	0.0009	0.1878	
CaO	0.40	56.08	0.0071	1
Na_2O	11.47	61.994	0.1850	
K_2O	0.20	94.2	0.0021	0.1942	

The empirical formula of albite is therefore:



HYDRATED COMPOUNDS

In determining the molecular formulas of crystalline chemical compounds, many of which contain water of crystallization, it is not only imperative that the percentage composition be given, but also the molecular weight must be known. The following example will serve to illustrate an alternate method of attack in establishing the true formula of a compound when the molecular weight of the substance has been previously determined.

Example.—A hydrated calcium phosphate contained 7.14 per cent water of crystallization. The molecular weight of this phosphate is 252.168. The percentage composition is

$$\begin{array}{ll} \text{Ca} = 15.89 \text{ per cent} & \text{P} = 24.60 \text{ per cent} \\ \text{H} = 2.40 \text{ per cent} & \text{O} = 57.11 \text{ per cent} \end{array}$$

What is the molecular formula of this compound?

Since 100 g. of this phosphate contains 15.89 g. of Ca,
1 gram-mol or 252.168 g. of phosphate contains

$$252.168 \times \frac{15.89}{100} = 40.069 \text{ g. of Ca}$$

Now, 40.069 g. of Ca = $40.069/40.08 = 1$ gram-atom of Ca.
Therefore, each molecule of the phosphate contains one Ca atom.

Likewise, 1 gram-mol, or 252.168 g., of phosphate contains
 $252.168 \times 2.40/100 \text{ g.} = 6.025 \text{ g. of H.}$
and

$$6.052 \text{ g. of H} = \frac{6.052}{1.008} = 6 \text{ gram-atoms of H}$$

1 gram-mol of phosphate contains $252.168 \times 24.60/100 \text{ g.} =$
62.033 g. of P, and $62.033/31.02 = 2$ gram-atoms of P.
and

$$1 \text{ gram-mol of phosphate contains } 252.168 \times \frac{57.11}{100} \times \frac{1}{16.00} = 9$$

gram-atoms of O.

The weight ratios of the various atoms, Ca:H:P:O = 1:6:2:9.

Since the phosphate contains 7.14 per cent water of crystallization, 1 gram-mol of the phosphate contains $252.168 \times 7.14/100$
 $\times 1/18.016 = 1$ gram-mol of H₂O.

The analysis gives the total hydrogen and oxygen content of the phosphate without regard to the water of crystallization, and only 1 gram-mol of H₂O is contained in the molecule. The salt must be an acid phosphate, since not all the hydrogen is combined with the oxygen to form water. Of the 6 atoms of hydrogen in the molecule, only 2 are combined with 1 oxygen atom, thus leaving 4 atoms of H and 8 atoms of O in the main body of the formula. So the molecular formula of the phosphate from the foregoing calculations is shown to be CaH₄P₂O₈.H₂O, or, preferably, Ca(H₂PO₄)₂.H₂O, which is the formula for monocalcium phosphate.

Problems

NOTE.—Answers are purposely omitted in almost every one of these problems.

- 346.** Derive the empirical formula of the substance that gave on analysis: 18.28 per cent Ca, 32.36 per cent Cl, 49.36 per cent H_2O .
- 347.** Derive the empirical formula of the compound of the following composition: 16.08 per cent K, 40.15 per cent Pt, 43.76 per cent Cl.
- 348.** Derive the empirical formula of the substance that gave on analysis: 30.75 per cent K, 25.21 per cent S, 44.04 per cent O.
- 349.** Derive the empirical formula of the substance that has the following percentage composition: 36.79 per cent N, 5.30 per cent H, 15.77 per cent C, 42.13 per cent S.
- 350.** Derive the empirical formula of the compound that gave on analysis: 75.07 per cent Al, 24.93 per cent C.
- 351.** Derive the empirical formulas of the substances from the following percentage composition:
- | | |
|--------------------------|--------------------------|
| (a) Fe = 27.929 per cent | (b) Fe = 36.761 per cent |
| S = 24.053 per cent | S = 21.106 per cent |
| O = 48.016 per cent | O = 42.132 per cent |
- 352.** Derive the empirical formulas of the substances that have the following percentage composition:
- | | |
|------------------------|------------------------|
| (a) K = 26.59 per cent | (b) K = 40.26 per cent |
| Cr = 35.39 per cent | Cr = 26.77 per cent |
| O = 38.02 per cent | O = 32.95 per cent |
- 353.** Derive the empirical formula of the substance that by analysis gave the following percentage composition: 69.94 per cent iron, 30.06 per cent oxygen.
- 354.** Derive the molecular formula of the substance that gave on analysis: 5.92 per cent hydrogen, 94.07 per cent oxygen. The molecular weight of the substance is 34.016.
- 355.** Derive the empirical formula of the substance that gave on analysis: 32.54 per cent K, 26.67 per cent S, 39.94 per cent O, 0.84 per cent H.
- 356.** Derive the empirical formula of the substance that gave on analysis: 16.63 per cent Si, 83.36 per cent Cl.
- 357.** A substance on analysis gave the following percentage composition: C = 10.05 per cent, H = 0.84 per cent, Cl = 89.10 per cent. Derive the empirical formula of the substance.
- 358.** Derive the molecular formula of the substance that by analysis gave: 2.24 per cent H, 26.6 per cent C, 71.09 per cent O. This compound has a molecular weight of 90.016.
- 359.** A hydrocarbon possesses the following percentage composition: C = 92.25 per cent, H = 7.75 per cent. Its vapor density is 13. Derive the molecular formula.
- 360.** A hydrocarbon, by analysis, gave the following percentage composition: C = 82.65 per cent, H = 17.35 per cent. Its vapor density is 29. Derive the molecular formula.

- 361.** A substance was found, by analysis, to contain: Na = 22.31 per cent, S = 31.10 per cent, O = 46.57 per cent. Its molecule is 102.24 times as heavy as the hydrogen molecule. Derive its molecular formula.
- 362.** An oxide of nitrogen contains 30.44 per cent N, 69.56 per cent O; 250 cc. of this gas reduced to standard conditions weighs 1.0268 g. Derive its molecular formula.
- 363.** Derive the molecular formula of that substance which contains: N = 12.27 per cent, H = 3.53 per cent, S = 28.09 per cent, O = 56.09 per cent. The substance has a molecular weight of 228.184.
- 364.** In an oxide of nitrogen, 8.363 g. of N is combined with 14.337 g. of O. The vapor density of this oxide of nitrogen is 38. Derive its molecular formula.
- 365.** An oxide of nitrogen contains 4.0185 g. of N combined with 11.4815 g. of O. The molecular weight of this oxide is 108. Derive its molecular formula.
- 366.** One liter of phosgene at 0°C. and 760 mm. pressure weighs 4.416 g. The percentage composition is: C = 12.13 per cent, O = 16.17 per cent, Cl = 71.69 per cent. Derive the formula of the substance.
- 367.** Hydrofluoric acid has the following percentage composition: 5.04 per cent H, 94.96 per cent F. Its molecule is 19.849 times as heavy as the hydrogen molecule. Derive the molecular formula of the acid.
- 368.** A chloride of mercury contains 50.55 g. of Hg combined with 8.935 g. of Cl. Its molecule is 234.186 times as heavy as the hydrogen molecule. Derive the molecular formula of the chloride.
- 369.** In two oxides of lead it is found that (a) 179.24 g. of Pb is combined with 20.76 g. of O; (b) 129.93 g. of Pb is combined with 20.07 g. of O. Derive the empirical formulas of these compounds.
- 370.** Chromium forms two oxides. In the acidic oxide 3.45 g. of Cr is combined with 3.184 g. of O. In the basic oxide 5.25 g. of Cr is combined with 2.423 g. of O. Derive the empirical formulas of these two oxides.
- 371.** A volume of an oxide of chlorine measuring 300 cc. and reduced to standard conditions weighs 0.9035 g. The percentage composition is: 52.56 per cent Cl, 47.43 per cent O. Derive the molecular formula of the oxide.
- 372.** A hydrocarbon has the following percentage composition: C = 92.25 per cent, H = 7.75 per cent. The vapor of this compound is 38.71 times as heavy as hydrogen. Derive the molecular formula of the compound.
- 373.** The following is the percentage composition of two organic substances:
(a) C = 52.12 per cent H = 13.13 per cent O = 34.74 per cent
(b) C = 42.08 per cent H = 6.48 per cent O = 51.43 per cent
The molecular weight of (a) is 46.048. That of (b) is 342.176. Derive the molecular formula of each of these compounds.
- 374.** Two hydrocarbons have the following percentage composition: C = 92.25 per cent, H = 7.75 per cent. One hundred cubic centi-

- meters of one of these hydrocarbons at 0°C. and 760 mm. weighs 0.1161 g. The vapor of the other hydrocarbon under like conditions is 3 times as heavy as the first. Derive the molecular formula of each substance.
- 375.** The percentage composition of an organic acid is: C = 39.96 per cent, H = 6.71 per cent, O = 53.30 per cent. Its molecule is 29.77 times as heavy as the hydrogen molecule. Derive the molecular formula of this acid.
- 376.** The following is the percentage composition of two organic substances: C = 54.51 per cent, H = 9.15 per cent, and O = 36.33 per cent. It was determined that 100 cc. of vapor of the simpler compound at 0°C. and 760 mm. pressure weighed 0.3931 g. The density of the other compound is twice that of the first. Derive the molecular formulas of both organic compounds.
- 377.** Three hydrocarbons have the following percentage composition: C = 85.61 per cent, H = 14.39 per cent. The molecule of the simplest of these hydrocarbons is 13.904 times as heavy as the hydrogen molecule. The molecule of the second compound is twice as heavy as the first. The molecule of the third hydrocarbon is twice as heavy as the second compound. Derive the molecular formula of each substance.
- 378.** The percentage composition of a volatile nitrogen compound follows: C = 46.15 per cent, N = 53.85 per cent. At standard conditions of temperature and pressure, 47 cc. of the vapor weighs 0.1092 g. Derive the molecular formula of this substance.
- 379.** The percentage composition of an organic solvent is: C = 62.029 per cent, H = 10.416 per cent, O = 27.555 per cent. At a temperature of 80°C. and 740 mm. pressure, 265.5 cc. of the vapor of this compound weighs 0.5182 g. Determine the molecular formula of this substance.
- 380.** An oxide of nitrogen has the following composition: N = 30.44 per cent, O = 69.56 per cent. At 140°C. and 755 mm. pressure, 228.5 cc. of this gas weighs 0.308 g. What is its molecular formula?
- 381.** An organic compound has the following percentage composition: C = 37.215 per cent, H = 7.815 per cent, Cl = 54.970 per cent. It was determined that 109 cc. of the vapor of this compound, measured at 21°C. and 750 mm. pressure, weighed 0.2879 g. Determine the molecular formula of this volatile compound.
- 382.** A volatile organic compound has the following composition: C = 24.259 per cent, H = 4.075 per cent, Cl = 71.665 per cent. It was found that 140.2 cc. of the vapor of this compound, measured at 100°C. and 740 mm. pressure, weighed 0.4416 g. What is the molecular formula of this substance?
- 383.** A rock, by analysis, gave the following composition: 12.19 per cent Na, 20.71 per cent K, 6.44 per cent Mg, 22.2 per cent Si, 38.15 per cent O. Derive the empirical formula.

- 384.** The percentage composition of a mineral was given as follows:

Lime, CaO	9.20 per cent
Alumina, Al_2O_3	16.79 per cent
Silica, SiO_2	59.21 per cent
Water.....	14.80 per cent

Derive the empirical formula of the mineral.

- 385.** The gem stone emerald has the following theoretical composition: 5.06 per cent Be, 10.05 per cent Al, 31.48 per cent Si, 53.40 per cent O. Derive the theoretical empirical formula of the mineral.

Ans. $3\text{BeO} \cdot 6\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ or $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$.

- 386.** The theoretical composition of kaolinite is: 46.59 per cent SiO_2 , 39.48 per cent Al_2O_3 , 13.92 per cent H_2O . Derive the empirical formula of this mineral.

- 387.** A specimen of cryolite analyzed by Hillebrand (U. S. Geol. Survey *Bull.* 591, p. 290) gave the following results: Al = 12.81 per cent, Na = 32.40 per cent, Ca = 0.28 per cent, F = 53.55 per cent, Fe_2O_3 = 0.40 per cent, H_2O = 0.30 per cent. Derive the empirical formula of the mineral.

Ans. Na_3AlF_6 .

- 388.** A specimen of garnet analyzed by Steiger (U. S. Geol. Survey *Bull.* 591, p. 311) gave the following results: SiO_2 = 38.59 per cent, Al_2O_3 = 22.24 per cent, Fe_2O_3 = 0.45 per cent, FeO = 0.36 per cent, MnO = 0.10 per cent, CaO = 35.97 per cent, MgO = 0.64 per cent, H_2O = 1.11 per cent, CO_2 = 0.39 per cent, F = 0.17 per cent. Derive the empirical formula of this mineral.

Ans. $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$.

- 389.** The mineral muscovite (mica) has the following theoretical composition: 20.36 per cent Al, 9.79 per cent K, 0.50 per cent H, 21.26 per cent Si, 48.08 per cent O. Derive the empirical formula of this mineral.

- 390.** A sample of colemanite (analysis by Whitfield, U. S. Geol. Survey *Bull.* 591, p. 346) has the following percentage composition: B_2O_3 = 49.56 per cent, CaO = 27.36 per cent, MgO = 0.25 per cent, H_2O = 22.66 per cent, SiO_2 = 0.44 per cent. Derive the empirical formula of this mineral.

Ans. $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ or $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$.

- 391.** A sample of meerschaum from New Mexico (analysis by Steiger, U. S. Geol. Survey *Bull.* 591, p. 340) gave the following analysis: SiO_2 = 57.10 per cent, Al_2O_3 = 0.58 per cent, Fe_2O_3 = trace, CaO = 0.17 per cent, MgO = 27.16 per cent, H_2O = 14.78 per cent, CO_2 = 0.32 per cent. Derive the empirical formula for meerschaum.

Ans. $(\text{MgO})_5(\text{SiO}_2)_7(\text{H}_2\text{O})_6$.

- 392.** When 10 g. of a salt of aluminum was heated, it was found to have lost 4.864 g. of water of crystallization. The percentage composition of the crystalline salt is: 8.13 per cent Al, 14.42 per cent S, 71.99 per cent O, 5.44 per cent H. Derive the empirical formula of the salt.

- 393.** Five grams of washing soda, upon heating, lost water of crystallization which amounted to 3.147 g. of its weight. The theoretical composition of the salt is: 16.07 per cent Na, 4.19 per cent C, 72.68 per cent O, 7.04 per cent H. Derive the empirical formula of the substance.

394. One gram of a crystallized salt of iron lost 0.1279 g. of water of crystallization upon dehydration. The theoretical percentage composition is 37.03 per cent K, 13.22 per cent Fe, 17.04 per cent C, 19.89 per cent N, 1.43 per cent H, 11.36 per cent O. Derive the empirical formula of the salt.

395. The percentage composition of four gaseous hydrocarbons is as follows:

(a) C = 74.858 per cent	H = 25.142 per cent
(b) C = 79.878 per cent	H = 20.122 per cent
(c) C = 92.252 per cent	H = 7.748 per cent
(d) C = 85.620 per cent	H = 14.380 per cent

The density in grams per liter at S.T.P. of each gas is: (a) 0.7167, (b) 1.3567, (c) 1.1708, (d) 1.2644. Derive the molecular formula of each hydrocarbon.

396. The percentage composition of (a) palmitic acid and (b) stearic acid is given as follows:

(a) C = 74.920 per cent	O = 12.484 per cent	H = 12.586 per cent
(b) C = 75.985 per cent	O = 11.253 per cent	H = 12.762 per cent

The molecular weight of each is (a) 256.256, (b) 284.288. Derive the molecular formula of each of these organic acids.

397. Derive the molecular formulas of two compounds of calcium, carbon and oxygen, whose percentage composition is as follows:

(a) Ca = 31.285 per cent	C = 18.746 per cent	O = 49.969 per cent
(b) Ca = 40.041 per cent	C = 11.996 per cent	O = 47.963 per cent

The molecular weight of (a) is 128.07, (b) 100.07.

398. Plaster of Paris (a) and gypsum (b) have the following compositions:

(a) Ca = 27.608 per cent	S = 22.089 per cent	O = 49.607 per cent
(b) Ca = 23.275 per cent	S = 18.622 per cent	O = 55.762 per cent
(a) H = 0.696 per cent		
(b) H = 2.341 per cent		

Plaster of Paris contains 6.26 per cent water of crystallization and has a molecular weight of 290.276. Gypsum contains 20.9 per cent water of crystallization and has a molecular weight of 172.162. Derive the true formulas of both these compounds.

399. The percentage composition of a crystallized sodium salt is

Na = 16.66 per cent	S = 23.19 per cent
H = 2.19 per cent	O = 57.96 per cent

The compound contains 13.05 per cent water of crystallization. The molecular weight of this substance is 138.024. Derive the molecular formula of this salt.

400. A crystallized organic acid contains 28.58 per cent water of crystallization. The theoretical composition of the compound is: H = 4.80

per cent, C = 19.04 per cent, O = 76.16 per cent. The molecular weight of the compound = 126.048. Derive the molecular formula of this substance.

- 401.** A crystallized sodium salt contains 39.72 per cent water of crystallization and has a molecular weight of 136.072. The theoretical composition of the salt is:

$$\begin{array}{ll} \text{Na} = 16.90 \text{ per cent} & \text{C} = 17.64 \text{ per cent} \\ \text{H} = 6.66 \text{ per cent} & \text{O} = 58.80 \text{ per cent} \end{array}$$

What is the molecular formula of this crystallized salt?

- 402.** A phosphate of sodium contains 60.35 per cent water of crystallization. The molecular weight of this phosphate is 358.22. The theoretical composition of this salt is:

$$\begin{array}{ll} \text{Na} = 12.84 \text{ per cent} & \text{P} = 8.66 \text{ per cent} \\ \text{H} = 7.03 \text{ per cent} & \text{O} = 71.47 \text{ per cent} \end{array}$$

Derive the molecular formula of this phosphate.

- 403.** It was found that a phosphate of sodium contained 23.09 per cent water of crystallization. The molecular weight of this phosphate is 156.068. The percentage composition was found to be:

$$\begin{array}{ll} \text{Na} = 14.74 \text{ per cent} & \text{P} = 19.87 \text{ per cent} \\ \text{H} = 3.87 \text{ per cent} & \text{O} = 61.52 \text{ per cent} \end{array}$$

What is the molecular formula of this salt?

CHAPTER VII

OUTLINE

The chemical equation.

The equation indicates the number of molecules that react (reactants) and the number of molecules of products (resultants) formed.

The mechanism of balancing an equation.

The equation represents facts. These facts can be derived from

a. Actual experimental tests.

b. Some general principles or laws.

The equation represents the weight ratios of the substances that react and of the products formed.

The equation represents the volume of any gas that is one of the reacting substances or of the products. The gram-molecular volume is 22.4 l. at S.T.P.

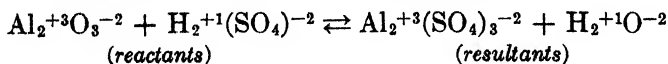
Summary of what the equation represents.

CHEMICAL EQUATIONS

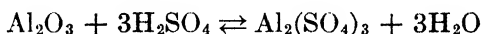
It is a familiar fact that when two or more substances react chemically to form new products there is no gain or loss in weight (Law of Conservation of Mass). The sum of the weights of the products of the reaction (resultants) is equal to the sum of the weights of the original substances (reactants). A chemical reaction or an experimental fact is conveniently represented by a chemical equation—a shorthand expression to represent the true facts, both qualitatively as well as quantitatively. In formulating a chemical equation let us consider the reaction between sulfuric acid and aluminum oxide. The experimental facts of this reaction can be represented by the following statement

Aluminum oxide + sulfuric acid \rightleftharpoons aluminum sulfate + water

Having at our command the symbols of the various elements and the various valence numbers associated with the individual atoms and radicals, the formulas of the compounds involved in the foregoing reaction can be set down as follows:



By inspection it is noted that each of the formulas of the reactants, and of the resultants, is correct. (That is to say, each element has its correct valence number assigned to it, and each formula is electrically balanced.) The equation is qualitatively complete. The reaction can be looked upon from this viewpoint: Aluminum can replace the hydrogen of sulfuric acid and combine with the SO_4 radical, forming the salt aluminum sulfate. The hydrogen, in turn, takes the place of the aluminum, forming water. Al, however, with a valence number of +3, can replace 3 H atoms; 2 Al atoms will, therefore, replace 6 H atoms. In order that sulfuric acid may furnish 6 H atoms, there must be 3 molecules of H_2SO_4 on hand. The number 3 is therefore placed as a coefficient to the H_2SO_4 , or $3\text{H}_2\text{SO}_4$. This coefficient governs the entire molecule of H_2SO_4 ; *i.e.*, $3\text{H}_2(\text{SO}_4)$ signifies $3 \times \text{H}_2$, or 6 H atoms; and $3 \times \text{S}$, or 3 S atoms; and $3 \times \text{O}_4$, or 12 O atoms, or $3 \times \text{H}_2$, or 6 H^{+1} atoms and 3 $(\text{SO}_4)^{-2}$ radicals. The 2 Al^{+3} atoms will unite with 3 $(\text{SO}_4)^{-2}$ radicals to form a molecule of $\text{Al}_2^{+3}(\text{SO}_4)_3^{-2}$. The 6 H^{+} atoms unite with 3 O^{-2} atoms to form 3 molecules of H_2O . Writing this as an equation:



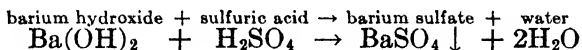
It is obvious that we arrange to have the same number of atoms of the same element on either side of our equation. That is, the equation is not only complete but also balanced. It represents the chemical facts as a result of experimentation.

It should again be emphasized that the experimental facts in any chemical reaction **must be known** before any chemical equation is formulated for the reaction. The student should not attempt to write the chemical equation for a chemical reaction unless he knows that the substances actually do react (undergo chemical changes) and knows the nature of the actual products formed. This knowledge may be the result of information on this specific reaction, or it may result from an application of the student's *general knowledge of this type of reaction*. The first alternative requires an immense amount of memory work. The second requires an ability to apply the principles of chemistry. The acquisition of this ability to "think chemically" is, of course, the main reason for giving any course in chemistry.

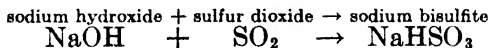
In our study of inorganic chemistry we come in contact with two distinct groups of chemical reactions. In the first group we have reactions involving simple metathesis or various types of double decomposition, and chemical union of basic oxides with acidic oxides. The second group comprises a more complicated type of reaction and is called oxidation and reduction. The main distinction between these two groups is that in the first group there are no changes in valence numbers of any of the elements involved in a chemical reaction, but in the second group certain elements in a chemical reaction undergo changes in valence numbers. This chapter will be concerned with reactions of the type classed as the first group. The next chapter will deal with reactions classed in the second group.

When confronted with the task of balancing a chemical equation, the student frequently makes the remark: "I could balance the equation if I knew what the products of the reaction were." There are some principles established by experiment that are beneficial to the student to aid him in determining the products of a chemical reaction. Some of these principles are:

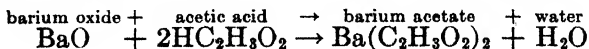
(a) Simple neutralization always involves the reaction between any acid and any base to form a salt of the acid and to form water,



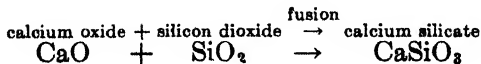
(b) An acid anhydride or acidic oxide (acid minus water) behaves like the parent acid from which it was derived; *i.e.*; sulfur dioxide, SO_2 , the anhydride of sulfurous acid, would react as this acid does.



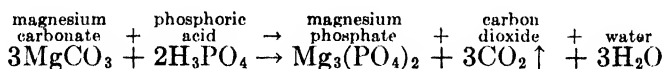
(c) A basic anhydride or basic oxide (base minus water) reacts like the base which it could form when added to water.



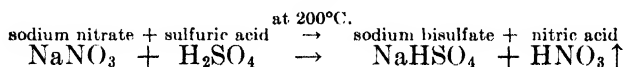
(d) The chemical union of a basic oxide and an acidic oxide forms a salt.



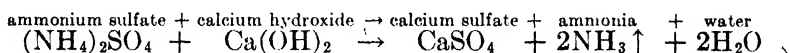
- ✓ (e) A carbonate acted upon by any acid always produces an effervescence of carbon dioxide, a salt of the acid used, and water.



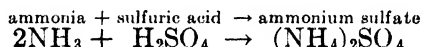
- (f) The formation of a volatile acid (low boiling point) results from the action of sulfuric acid or phosphoric acids (both non-volatile acids) on a salt of the volatile acid.



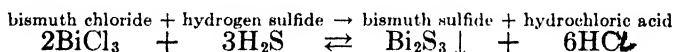
- (g) When an ammonium salt is heated with a nonvolatile base, ammonia is always released.



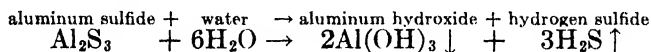
- (h) Ammonia added to any acid forms an ammonium salt of that acid.



- (i) Hydrogen sulfide passed into solutions of many heavy metal salt solutions produces insoluble sulfides.



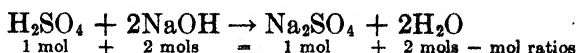
- (j) Hydrolysis or hydrolytic actions in which water plays the role of a chemical reagent is here exemplified:



or

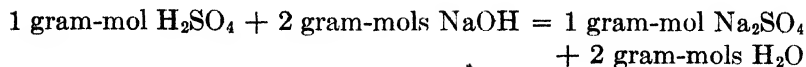


In addition to representing the number of molecules that react, a chemical equation also indicates the weight ratios of the substances that react; thus, when sulfuric acid is completely neutralized by sodium hydroxide, the equation is written:

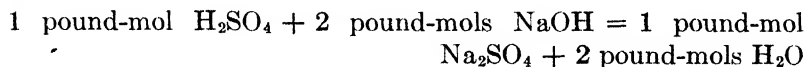


Since the mol ratios represent the relative weights of molecules

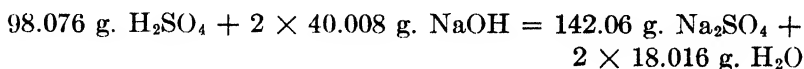
(parts by weight), these weights can be expressed in any convenient quantity unit such as grains, grams, kilograms, ounces, pounds, or tons. Thus,



or



or



In the case of chemical reactions involving gases, it is customary to deal with the equation in which the mol ratios are expressed directly in terms of volume ratios instead of weight ratios. From facts learned in Chap. V, a gram-mol of any gas occupies 22.4 l. at S.T.P. (molar volume), or 1 kilogram-mol of any gas occupies 22.4 cu. m. at S.T.P. Also 1 ounce-mol of any gas occupies 22.4 cu. ft. at S.T.P., or 1 lb.-mol of any gas occupies 358.4 cu. ft. at S.T.P.

Summarizing, the chemical equation represents:

(a) The substances that react (reactants) and the products formed (resultants).

(b) The relative number of molecules of reactants and of resultants involved (mol ratios).

(c) The relative weights (atomic and molecular) of reactants and of resultants (weight ratios).

(d) The volume ratios of gases at S.T.P. involved in a reaction.

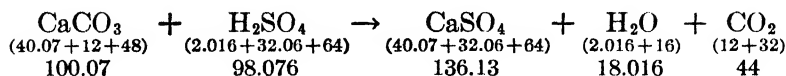
Example.—A 1-g. sample of marble that contains 99.5 per cent CaCO_3 is treated with dilute sulfuric acid, specific gravity 1.20 and containing 27.32 per cent by weight of H_2SO_4 . Calculate:

(a) The number of cubic centimeters of this sulfuric acid needed for complete chemical action.

(b) The weight of calcium sulfate formed.

(c) The volume of carbon dioxide liberated at standard conditions.

The equation representing the action involved in this problem is



parts by weight, such as grams, ounces, tons, kilograms.

Since the marble is 99.5 per cent pure CaCO_3 , the 1-g. sample will actually contain 0.995 g. of CaCO_3 .

100.07 g. of CaCO_3 is contained in 1 gram-mol of CaCO_3

0.995 g. of CaCO_3 is contained in $0.995/100.07 = 0.00994$ gram-mol of CaCO_3 .

(a) The equation shows that

1 gram-mol of CaCO_3 reacts with 1 gram-mol of H_2SO_4 or 98.076 g. H_2SO_4

0.00994 gram-mol of CaCO_3 will react with 0.00994×98.076 g. or 0.975 g. of H_2SO_4 .

The specific gravity of the sulfuric acid solution is 1.2 and contains 27.32 per cent by weight of H_2SO_4 . That is, 1 cc. of this acid weighs 1.2 g.; and since this acid is 27.32 per cent pure, the actual weight of active H_2SO_4 in 1 cc. is $1.2 \times 0.2732 = 0.3278$ g. of active H_2SO_4 .

Then there will be

$$1 \text{ g. of } \text{H}_2\text{SO}_4 \text{ in } \frac{1}{0.3278} \times 1 \text{ cc. of sulfuric acid solution}$$

$$0.975 \text{ g. of } \text{H}_2\text{SO}_4 \text{ in } 0.975 \times \frac{1}{0.3278} \times 1 \text{ cc.} = 2.97 \text{ cc.}$$

of sulfuric acid (sp. gr. 1.2 and 27.32 per cent by weight of H_2SO_4). Or, 2.97 cc. of the acid solution will be needed to react completely with the 1-g. sample of marble.

(b) The foregoing equation states that

1 gram-mol of CaCO_3 forms 1 gram-mol of CaSO_4 , or 136.13 g. of CaSO_4 ; then 0.00994 gram-mol of CaCO_3 forms $0.00994 \times 136.13 = 1.353$ g. of CaSO_4 .

(c) Since one gram-molecular weight (1 gram-mol) of any gas occupies 22.4 l. at standard conditions (molar volume), then one gram-molecular weight of CO_2 , or 44 g., will occupy 22.4 l. at standard conditions. From the equation,

1 gram-mol of CaCO_3 yields 22.4 l. of CO_2 at S.T.P.

0.00994 gram-mol of CaCO_3 will yield $0.00994 \times 22.4 = 0.223$ l., or 223 cc. of CO_2 at S.T.P.

Problems

The first requirement in each of the following problems is the chemical equation involved. This is to be properly completed and balanced before attempting to make any calculations.

404. Prussian blue, $\text{Fe}_4(\text{Fe}(\text{CN}_6))_3$, is obtained by the reaction between ferric chloride and potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN}_6)$. What weight of Prussian blue is produced from 100 lb. of ferric chloride by this reaction?
Ans. 132.3 lb.
405. Calculate (a) the amount of quicklime that can be produced from 7 tons of limestone which analyzed 96.5 per cent CaCO_3 . (b) How many bags, each containing 50 lb. of hydrated lime, $\text{Ca}(\text{OH})_2$, can be obtained from the amount of quicklime produced in (a).
Ans. (a) 3.782 tons; (b) 200 bags.
406. Calculate the weight of lead chromate that is produced by the addition of a solution containing 50 g. of $\text{K}_2\text{Cr}_2\text{O}_7$ to a solution containing an excess of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.
Ans. 109.84 g.
407. A sample of hard water contains 0.22 g. of CaSO_4 and 0.255 g. of MgSO_4 per gallon. Calculate the weight of Na_2CO_3 necessary to precipitate the calcium and magnesium salts from 5,000 gal. of water.
Ans. 1,979 g.
408. An excess of NaNO_3 is treated with 25 lb. of sulfuric acid which contains 93.19 per cent by weight of H_2SO_4 . Calculate (a) the number of pounds of nitric acid containing 70 per cent by weight of HNO_3 that is produced by this action; (b) the weight of Na_2SO_4 also obtained.
Ans. (a) 42.76 lb.; (b) 33.74 lb.
409. Calculate the weight of sodium nitrate containing 89.5 per cent NaNO_3 necessary to produce 50 tons of nitric acid containing 65.3 per cent by weight of HNO_3 .
Ans. 49.21 tons.
410. How many cubic centimeters of sulfuric acid (sp. gr. 1.8354 and containing 93.19 per cent by weight of H_2SO_4) will be required to neutralize completely 25 cc. of sodium hydroxide solution, specific gravity 1.345 and containing 31.22 per cent by weight of NaOH ?
Ans. 7.52 cc.
411. How many cubic centimeters of potassium hydroxide solution (sp. gr. 1.252 and containing 27.0 per cent by weight of KOH) will be required to neutralize completely 15 cc. of hydrochloric acid, specific gravity 1.20 and containing 39.8 per cent by weight of HCl ?
Ans. 32.59 cc.
412. Calculate the theoretical ratio by weight of magnesium nitride to hot water necessary for complete chemical action?
Ans. 1:1.07.
413. (a) Calculate the weight of slaked lime required to liberate all the ammonia from 1 ton of $(\text{NH}_4)_2\text{SO}_4$. (b) What volume of NH_3 is liberated at standard conditions?
Ans. (a) 1,121 lb.; (b) 10,850 cu. ft.

414. Calculate (a) the volume of sulfuric acid (sp. gr. 1.83 and containing 92.1 per cent by weight of H_2SO_4) necessary to completely react with 100 lb. of borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, to form boric acid. (b) Calculate the weight of boric acid formed. *Ans.* (a) 1.827 gal.; (b) 64.8 lb.
415. Calculate the weight of ferrous sulfide containing 95 per cent FeS that will be required to produce 2.5 cu. ft. of hydrogen sulfide at 21°C . and 750 mm. pressure. *Ans.* 0.59 lb.
416. Calculate the volume of hydrogen sulfide, at standard conditions, needed to precipitate completely CuS from 100 cc. of a solution that contains 0.75 g. of CuCl_2 in 1,000 cc. of solution. *Ans.* 12.4 cc.
417. Calculate the weight of sodium dichromate that can be obtained by adding the requisite amount of concentrated sulfuric acid to a solution containing 100 lb. of sodium chromate. *Ans.* 80.8 lb.
418. Determine the number of cubic feet of H_2S at 21°C . and 755 mm. pressure that will be required to produce 100 lb. of cadmium yellow, CdS , from an excess of $\text{Cd}(\text{NH}_3)_4\text{SO}_4$. *Ans.* 270 cu. ft.
419. Calculate (a) the volume of CO_2 , at standard conditions, that is necessary to saturate completely 50 cc. of ammonium hydroxide solution (sp. gr. 0.90 and containing 28.3 per cent by weight of NH_3). (b) Calculate, also, the weight of ammonium bicarbonate obtained by the reaction. *Ans.* (a) 16.75 l.; (b) 59.20 g.
420. (a) Calculate the number of cubic centimeters of hydrochloric acid (sp. gr. 1.115 and containing 22.86 per cent by weight of HCl) necessary to react with 90 cc. of a silver nitrate solution containing 40.6 g. of silver ion in 1 l. of solution. (b) Calculate the weight of AgCl produced. *Ans.* (a) 4.84 cc.; (b) 4.85 g.
421. How many cubic centimeters of a silver nitrate solution (sp. gr. 1.1404 and containing 15 per cent by weight of AgNO_3) is necessary to react with 40 cc. of hydrochloric acid having a specific gravity of 1.14 and containing 27.66 per cent by weight of HCl? *Ans.* 343.8 cc.
422. Calculate (a) the volume of ammonia, (b) the volume of CO_2 (both gases at standard conditions) necessary to prepare sufficient ammonium carbonate to react with 22 g. of SrCl_2 . *Ans.* (a) 6.2 l. NH_3 ; (b) 3.1 l. CO_2 .
423. Calculate the volume of sulfuric acid solution (sp. gr. 1.8374 and containing 94.4 per cent by weight of H_2SO_4) necessary to convert completely 3.427 g. of PbCl_2 into PbSO_4 . *Ans.* 0.70 cc.
424. How many cubic centimeters of ammonium acetate solution, containing 4.283 g. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ per 100 cc., will be necessary to react completely with 1.092 g. of PbSO_4 ? *Ans.* 12.96 cc.
425. (a) Calculate the number of cubic centimeters of sulfuric acid solution (sp. gr. 1.7649 and containing 83 per cent by weight of H_2SO_4) necessary to dissolve 6 g. of basic zinc carbonate, $\text{Zn}_2(\text{OH})_2(\text{CO}_3)_2$. (b) What volume of CO_2 , at standard conditions, is produced? *Ans.* (a) 3.66 cc. H_2SO_4 ; (b) 489.7 cc. CO_2 .
426. A precipitate of barium chromate weighing 4.270 g. is treated with 5 cc. of hydrochloric acid (sp. gr. 1.185 and containing 36.31 per cent

by weight of HCl). By calculations, show that all the BaCrO_4 will dissolve.

427. Calculate the weight of Ag_2O obtained when 27.2 cc. of silver nitrate solution containing 18 g. AgNO_3 per 100 cc. is treated with excess sodium carbonate. *Ans.* 3.339 g. Ag_2O .
428. A sample of a ferric salt contains 20.3 per cent Fe. In a chemical analysis 0.42 g. of this sample is treated so that the iron is all changed into ferric chloride. Calculate the number of cubic centimeters of ammonium hydroxide solution (sp. gr. 0.954 and containing 11.6 per cent by weight of NH_3) required to precipitate completely the iron as ferric hydroxide. *Ans.* 0.7 cc.
429. Calculate the number of cubic centimeters of ammonium hydroxide solution (sp. gr. 0.924 and containing 20.5 per cent by weight of NH_3) that can be prepared from a solution containing 2,000 g. of ammonium sulfate. *Ans.* 2,719 cc.

Additional Problems without Answers, for Quizzes

430. What is the formula for the salt produced when 2.68 l. of SO_2 (S.T.P.) reacts with 4.446 g. of Ca(OH)_2 ?
431. If 1.453 l. of CO_2 measured at 21°C . and 758 mm. reacts with 2.223 g. Ca(OH)_2 , what is the formula of the salt produced?
432. If 0.132 g. of calcium hydroxide is allowed to react with 0.3497 g. of phosphoric acid, what is the formula of the salt formed?
433. What is the formula of the salt formed by the reaction of 1.653 g. of RbOH with 1.581 g. of H_2SO_4 ?
434. How many grams of H_2O is obtained when 3.3 g. Ca(OH)_2 react with 8.73 g. of H_3PO_4 ?
435. Calculate the volume of sulfuric acid that has a specific gravity of 1.25 and contains 33.4 per cent by weight of H_2SO_4 , necessary to form 10 g. of NaHSO_4 by reaction with NaOH .
436. How many cubic centimeters of hydrochloric acid (sp. gr. 1.20 and containing 39.11 per cent by weight of HCl) will be required for the production of 10 l. of hydrogen sulfide gas collected at 21°C . and 745 mm. pressure, by action on FeS .
437. Calculate the number of cubic centimeters of microcosmic salt solution containing 50 g. of $\text{NaNH}_4\text{HPO}_4$ per liter that will be required to precipitate completely the magnesium in an ammoniacal solution containing 1 g. of MgCl_2 .
438. Calculate (a) the volume of sulfur dioxide in cubic feet, at 22°C . and 750 mm. pressure, that will be required to react completely with a solution of caustic soda containing 100 lb. of sodium hydroxide which is 75 per cent NaOH . (b) What weight of Na_2SO_3 is obtained?
439. (a) How much caustic soda, 92.5 per cent NaOH , is required to make 4 l. of sodium hydroxide solution having a specific gravity of 1.370 and containing 33.73 per cent by weight of NaOH ? (b) How many cubic centimeters of this caustic soda solution will be required to react com-

- pletely with 1,000 g. of ammonium sulfate? (c) How many liters of ammonia, at standard conditions, will be produced in this reaction?
440. (a) How much quicklime, 90 per cent CaO , is necessary to react completely with 1 l. of sodium carbonate solution having a specific gravity of 1.125 and containing 11.81 per cent by weight of Na_2CO_3 ? (b) How many grams of caustic soda will be produced in this reaction?
441. A caustic soda solution is prepared by dissolving 200 g. Na_2CO_3 in 3 l. of water and then adding 100 g. of commercial lime containing 90 per cent CaO . What weight of NaOH will be contained in 1 l. of this solution?
442. Determine the number of cubic centimeters of sulfuric acid (sp. gr. 1.83 and containing 92.10 per cent by weight of H_2SO_4) that will be required to react with 100 g. of $\text{Ca}_3(\text{PO}_4)_2$ to form primary calcium phosphate.
443. A quantity of limestone, 97.5 per cent CaCO_3 , is acted upon by dilute hydrochloric acid. By this action 1 cu. ft. of carbon dioxide at 70°F . and 30.7 in. Hg was obtained. Calculate the weight of limestone that was necessary for this action.
444. (a) A fire extinguisher contains $1\frac{1}{2}$ lb. of sodium bicarbonate. What volume of sulfuric acid (sp. gr. 1.83 and containing 92.10 per cent by weight of H_2SO_4) will be required to interact with this amount of sodium bicarbonate in the formation of sodium bisulfate? (b) What volume in cubic feet of CO_2 will be liberated, at S.T.P., by this action?
445. What volume of CO_2 , at 21°C . and 758 mm. pressure, passed into a suspension of calcium carbonate in water containing 5 g. of CaCO_3 , will be required to convert the insoluble calcium carbonate into the soluble calcium bicarbonate?
446. Calculate the weight of barium peroxide that will be necessary for the preparation of 100 cc. of hydrogen peroxide solution having a specific gravity of 1.15 and containing 30 per cent by weight of H_2O_2 .
447. Calculate the number of cubic centimeters of hydrofluoric acid (sp. gr. 1.15 and containing 48 per cent by weight of H_2F_2) required to react completely with 0.965 g. of silica, SiO_2 .
448. Sodium bisulfite is prepared by passing SO_2 into caustic soda solution, NaOH . Calculate the volume of sulfur dioxide, at standard conditions, that is necessary to prepare 100 cc. of sodium bisulfite solution having a specific gravity of 1.286 and containing 35.31 per cent by weight of NaHSO_3 .
449. Calculate the weight of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ that will be required to react with the calcium bicarbonate in 1,000,000 gal. of water that contains 0.015 per cent by weight of $\text{Ca}(\text{HCO}_3)_2$.
450. Calculate the number of gallons of waterglass (sp. gr. 1.394 and containing 37.9 per cent by weight of Na_2SiO_3) that can be obtained from the fusion of 1 ton of sand (99.5 per cent SiO_2) with excess anhydrous sodium carbonate, Na_2CO_3 , and subsequent solution in water.
451. Calculate the weights of sand (99.5 per cent SiO_2) and anhydrous sodium carbonate, Na_2CO_3 , that when fused and the resultant sodium

- silicate dissolved in water, will yield 100 gal. of waterglass (sp. gr. 1.394 and containing 37.9 per cent by weight of Na_2SiO_3).
452. Calculate the volume of phosphine, PH_3 , measured at 21°C . and 750 mm. pressure that will be obtained by the action of water on 100 g. of calcium phosphide, Ca_3P_2 .
453. Calculate the number of cubic centimeters of barium chloride solution containing 50 g. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per liter necessary to react completely with 10 g. of anhydrous sodium sulfate.
454. How many cubic centimeters of phosphoric acid (sp. gr. 1.333 and containing 50 per cent by weight of H_3PO_4) is required to react completely with NaOH in order to obtain 1 kg. of monosodium phosphate?
455. A two-fluid type of fire extinguisher employs a solution of $\text{Al}_2(\text{SO}_4)_3$ and a solution of NaHCO_3 that contains extract of licorice. When the two solutions are mixed, a reaction produces a foam consisting of aluminum hydroxide with CO_2 (the licorice serves to stabilize the foam). Calculate the amount of NaHCO_3 that will be required to react completely with 5 lb. of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in one of these extinguishers.
456. It is necessary to use 65 cc. of a NaOH solution to neutralize 100 cc. of an HCl solution containing 0.0016 g. of HCl per cubic centimeter. How many grams of NaOH would be required to prepare 1 l. of the same concentration?
457. How many cubic centimeters of NH_4OH (sp. gr. 0.93 and containing 18 per cent by weight of NH_3) is required to dissolve 10 g. of AgCl , assuming a straightforward reaction to give $\text{Ag}(\text{NH}_3)_2\text{Cl}$?
458. In the preparation of calcium carbide, CaC_2 , from CaO and C , how many tons of coke (100 per cent C) is required to convert 1 ton of CaO to CaC_2 , if 65 per cent of the carbon added is effective in the reaction?
459. If 100 g. of copper was dissolved in sulfuric acid to give 251.1 g. of CuSO_4 , and this was subsequently converted to $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ by addition of excess NH_4OH , how much $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ could be obtained if the recovery is 85 per cent of the theoretical amount?

CHAPTER VIII

OUTLINE

Definition of oxidation and reduction.

Oxidizing and reducing agents. Definitions. Table.

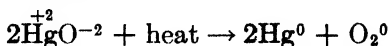
Mechanism of balancing oxidation-reduction equations.

Summary of method. Several examples to illustrate method here used.

OXIDATION-REDUCTION

In Chap. VII chemical reactions were represented by chemical equations in which there were no changes in valence numbers of any elements involved, and typical problems were confined to this type of chemical equation. The purpose of this chapter is to give special consideration to that group of chemical reactions in which the equation shows that two elements undergo changes in valence. That is, one element has its valence number increased (*oxidation*) while another simultaneously has its valence number decreased (*reduction*). A vast number of reactions are of this type, and they are classified as **oxidation-reduction** reactions. This type of equation is more complicated than those described previously; and to complete and balance it requires more skill and certainly more chemical knowledge on the part of the student. Let us consider a few simple examples to illustrate the principle of oxidation-reduction.

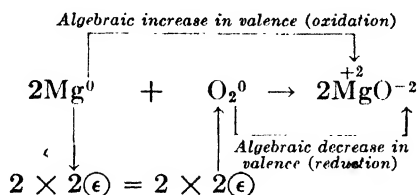
a. Simple decomposition: It is demonstrated in the chemical laboratory that strongly heating mercuric oxide yields free mercury and that oxygen escapes.



In this equation we note that the *valence number* of mercury is *decreased* from +2 to zero (reduction) and that the *valence number* of oxygen is *increased* from -2 to zero (oxidation). These changes in valence numbers are brought about in the following manner: The oxide ion gives up its 2 electrons to the mercuric ion, thereby neutralizing the positive charge (+2)

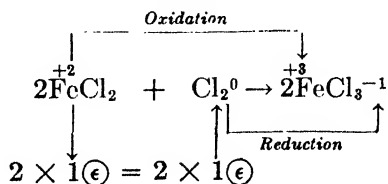
on this ion and forming metallic mercury (*zero valence number*). At the same time neutral oxygen atoms (*zero valence number*) are formed. Then two oxygen atoms unite with each other, forming molecular oxygen, which escapes. In order that we may have 2 oxide ions in the formation of molecular oxygen (O_2), it is necessary to take 2 molecules of HgO , which also yields 2 atoms of free mercury, as indicated.

b. Combination, or chemical union, illustrated by the burning of magnesium in the air to form magnesium oxide.

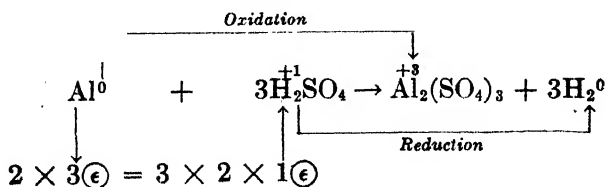


Note that the electron is symbolized as €, and the arrow under the Mg atom pointing downward (\downarrow) over it designates a *loss of electrons* (oxidation). Also, the arrow over the electron pointing upward under the oxygen indicates a *gain of electrons* by the oxygen (reduction).

c. The oxidation of ferrous chloride to ferric chloride by chlorine is represented by the following equation:



d. Ionic displacement reactions exemplified by the action of aluminum with dilute sulfuric acid.



Many more examples of simple oxidation-reduction equations are available, but those presented above will permit the following statements to be made:

(a) **Oxidation** is a process that involves the loss of electrons by an element resulting in an algebraic increase in the valence number of that element.

(b) **Reduction** is a process that involves the gain of electrons by an element resulting in an algebraic decrease in the valence number of that element.

The two processes oxidation and reduction always occur simultaneously in a reaction in which there are any changes of valence numbers of elements; neither process can occur without the other. When there is no change in valence numbers of the elements, the process does not involve oxidation or reduction.

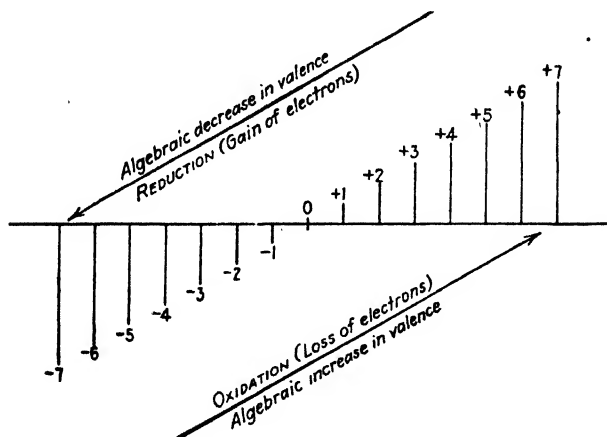


FIG. 14.—Valence scale.

The preceding figure (Fig. 14) will be of assistance in differentiating the changes in valence numbers in reactions involving *oxidation* and *reduction*.

Substances that are *electron acceptors* are called **oxidizing agents**, or simply **oxidizers**.

Substances that are *electron donors* are called **reducing agents**, or simply **reducers**.

Among the most common active oxidizers we have the halogens Cl_2 , Br_2 , and I_2 , H_2SO_4 , HNO_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, H_2O_2 , Na_2O_2 .

MnO_2 , $\text{Fe}_2(\text{SO}_4)_3$. All these substances contain an atom or ion that readily gains electrons.

Some common reducers are H_2 , H_2S , HI , HBr , FeCl_2 , H_2SO_3 , SnCl_2 , $\text{H}_2\text{C}_2\text{O}_4$, Na , Zn , Al . All these substances contain an atom or ion that readily gives up electrons.

In the following table of oxidizing and reducing powers of substances, the atom that gives up electrons (reducing agent) is indicated by the arrow pointing downward (\downarrow), and the atom that takes on electrons (oxidizing agent) by the arrow pointing upward (\uparrow).

TABLE X
OXIDIZERS (ELECTRON ACCEPTORS)

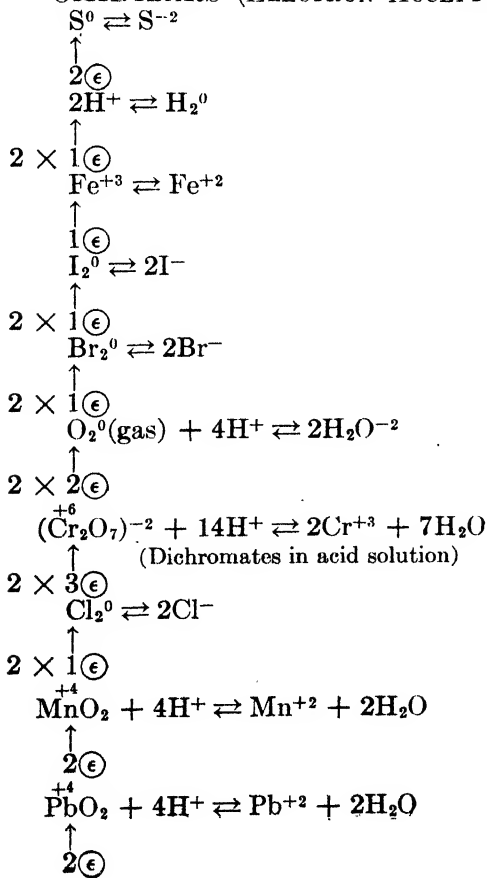
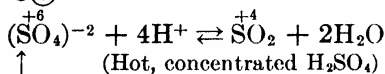
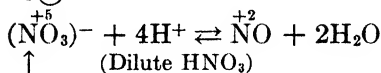
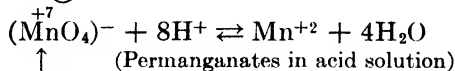
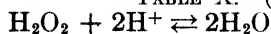


TABLE X.—(Continued)



—————→
REDUCTION

REDUCERS (ELECTRON DONORS)

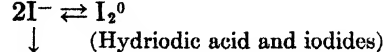
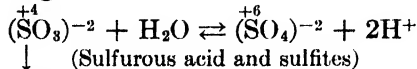
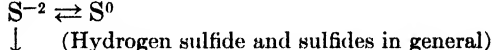
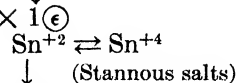
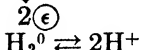
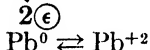
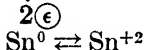
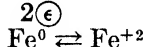
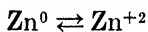
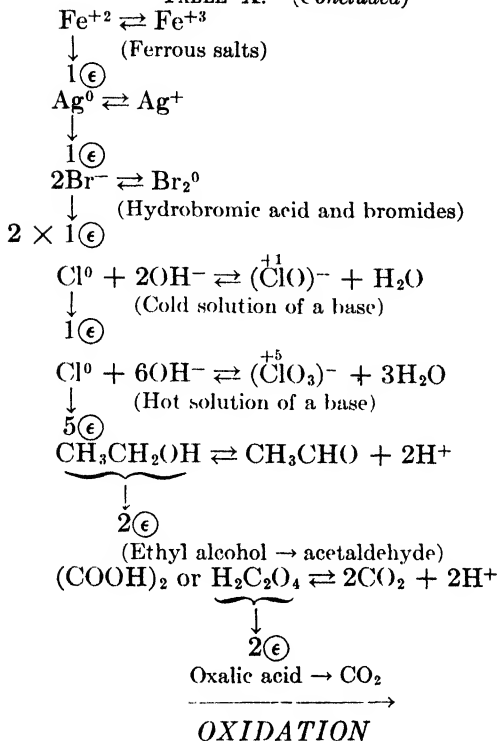
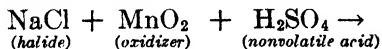


TABLE X.—(Concluded)



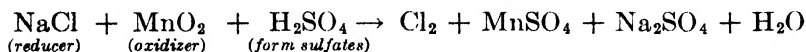
METHOD OF BALANCING OXIDATION AND REDUCTION EQUATIONS

In the study of the halogens—chlorine, bromine, and iodine—the student is confronted with a number of complicated equations, especially in the preparation of these halogens from their halides. The general statement is made at the outset that if one adds to a halide (fluorides excepted) a nonvolatile acid (sulfuric acid or phosphoric acid) and an oxidizer, the halogen will be liberated. Let us consider an equation representing this type of reaction.

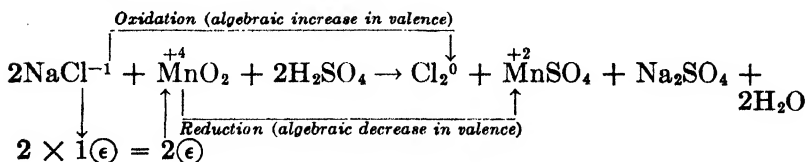


To complete this equation, we must first set down the products established by experiment. The facts are that chlorine will be liberated, and, from the table of oxidizing agents and reducing

agents, the oxidizer, MnO_2 , in the presence of H^+ is changed to Mn^{+2} , and H_2O is formed. It should also be noted that sulfuric acid not only furnishes H^+ ions but supplies sulfate ions (SO_4^{-2}) as well, thereby forming sulfates of various positive or metallic ions present in the reaction. All these facts can be written down:

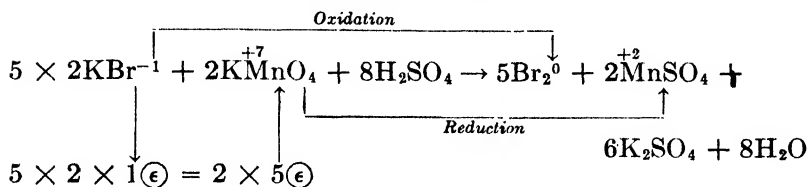


Next, note and indicate the changes in valence numbers and the electron transfer. In the beginning it helps the student if he draws an overhead bridge to indicate the *algebraic increase in valence number-oxidation* and an underslung bridge to indicate the *algebraic decrease in valence number-reduction* and uses the arrows under the reducer and oxidizer to show the number of electrons lost and gained, respectively. These numbers are determined by *noting the total change in valence in each case; i.e.*, if chloride ion (Cl^-) changes from -1 to 0 , this is a total change of 1 . One electron (1e^-) is lost. At the same time the manganese in MnO_2 changes from $+4$ to $+2$, a total change of 2 . Thus 2e^- are gained by the manganese to form manganous ion, Mn^{+2} . Next, *establish an electron balance by placing coefficients before the reducer and the oxidizer so that the number of electrons lost (by the reducer) equals the number gained (by the oxidizer)*. Incidentally, this will give corresponding coefficients of several products of the reaction. Finally, complete the balancing of the equation by inspection. All the foregoing steps can be combined and written in the form of the following molecular equation:



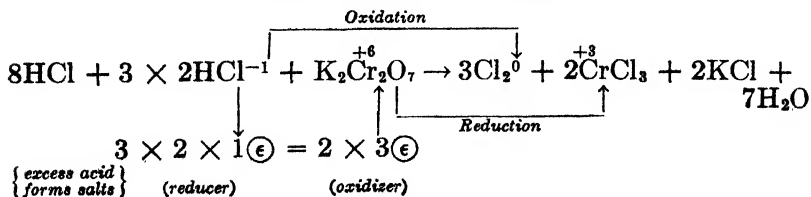
Further to illustrate this method of equation writing, consider the equation representing the oxidizing action of potassium permanganate, KMnO_4 , on potassium bromide and sulfuric acid. It should first be noted that the permanganate ion, MnO_4^- , in the presence of hydrogen ions, H^+ , actually oxidizes

the bromide ion, Br^- , and that potassium ions, K^+ , and sulfate ions, SO_4^{-2} , are incidental to the reaction. Employing the procedure previously outlined, the complete equation is set up, showing the reactants and the resultants. The valence changes are next noted and indicated together with the electron transfer. The electron balance is then established by choosing the proper coefficients of oxidizer and reducer. Finally, the balancing of the equation by inspection is undertaken.



From this equation one learns that the mol ratio of the reducer to the oxidizer is $10\text{KBr}:2\text{KMnO}_4$ or $5\text{Br}^-:1\text{MnO}_4^-$. That is to say, for every 5Br^- it requires 1MnO_4^- for complete oxidation-reduction.

Another equation that is somewhat troublesome to complete and balance is the equation representing the oxidizing action of potassium dichromate with an excess of concentrated hydrochloric acid. We note, from Table X, that the dichromate ion $\text{Cr}_2\text{O}_7^{-2} + \text{H}^+$ is reduced to chromic ion, Cr^{+3} . This represents a change in valence number for each chromium atom from $+6$ to $+3$. There are 2 chromium atoms in one $\text{Cr}_2\text{O}_7^{-2}$, and each of these 2 chromium atoms gains 3€ per atom, or a total gain of 6€ per $\text{Cr}_2\text{O}_7^{-2}$ ion, thereby forming 2 chromic ions, 2Cr^{+3} . It was stated that the hydrochloric acid is in excess, and it furnishes the H^+ ions necessary for the reaction to proceed. A part of the hydrochloric acid is oxidized to free chlorine, Cl_2 , by the dichromate ion. The remainder of the HCl furnishes the necessary chloride ions, Cl^- , to form salts, KCl and CrCl_3 . All this can be represented by the following molecular equation:



Note that hydrochloric acid really plays a dual role in this equation. It acts as a reducer and as an ordinary acid to form salts. Also, a total of 14 mols of HCl is required for the reaction, and only 6 mols is oxidized, the remaining 8 mols furnishing the necessary 8Cl^{-1} to form 2CrCl_3 and 2KCl .

The mol ratio of reducer:oxidizer in this equation is $6\text{Cl}^{-1} : 1\text{Cr}_2\text{O}_7^{-2}$.

SUMMARY OF METHOD

(a) Set down the complete equation showing products established as experimental facts.

(b) Determine which elements undergo a change in valence number, and indicate which element is oxidized and which is simultaneously reduced.

(c) Indicate the numerical change in valence numbers of the various atoms involved and the numbers of electrons involved in the transfer.

(d) Establish the electron balance by choosing coefficients or numbers of molecules of the reducer and of the oxidizer so that the number of electrons lost by the reducer is equal to the number gained by the oxidizer. An equals sign (=) can be conveniently placed between these numbers to show the electron balance.

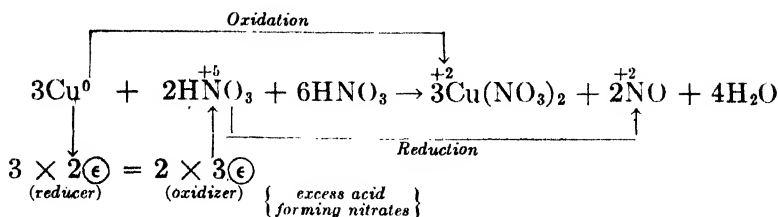
(e) By inspection, balance the rest of the equation.

The application of the method of completing and balancing equations, just described, to other types of oxidation-reduction reactions will now be given consideration.

ACTION OF DILUTE NITRIC ACID AS AN OXIDIZER

The Reaction of Dilute Nitric Acid with Metals.—Referring to Table X, we see that dilute nitric acid is an oxidizer. When dilute nitric acid acts on many metals, the nitrate ion, $(\text{NO}_3)^{-}$,⁺⁵ is reduced with the subsequent decrease in the valence number of the nitrogen atom from +5 to +2 (by the gain of 3 e), resulting in the formation of nitric oxide, NO. As a typical example, consider the reaction of dilute nitric acid with metallic copper. The copper, originally in the zero-valence condition (all free elements have zero valence), is oxidized to the cupric

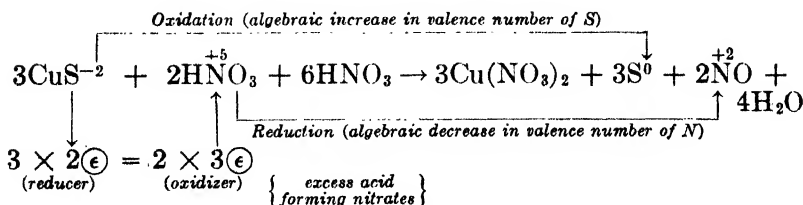
state, with valence number of $+2$, by the loss of 2 € , thus forming cupric ions, Cu^{+2} .



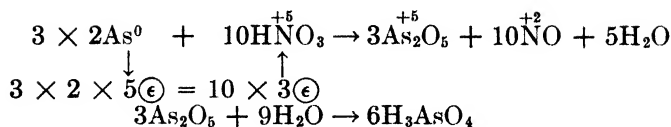
Note that dilute nitric acid has a dual role in this type of reaction: 2 mols of HNO_3 function as an oxidizer, and 6 mols of HNO_3 furnish 6NO_3^- which becomes associated with 3Cu^{+2} to form $3\text{Cu}(\text{NO}_3)_2$.

The Reaction of Dilute Nitric Acid with Metallic Sulfides.—

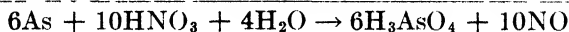
Reactions of this type can be exemplified in the case of the oxidation of cupric sulfide by dilute nitric acid. Reference to Table X gives the information that the sulfide ion, S^{-2} , is a reducer and when oxidized yields free sulfur, S^0 , by the loss of 2 € per ion with the accompanying change in valence number from -2 to zero (oxidation). This free sulfur will be visible and should be observed. The nitrate ion, NO_3^- , from the dilute nitric acid, is simultaneously reduced to NO ; the valence number of the nitrogen atom in the nitrate ion ($+5$) is decreased to $+2$ by the gain of 3 € (reduction). With this information at hand, the molecular equation can be written



The Reaction of Dilute Nitric Acid with Nonmetals.—When a nonmetal like phosphorus or arsenic is treated with dilute nitric acid, the products are phosphoric acid and arsenic acid, respectively, and nitric oxide. Thus,



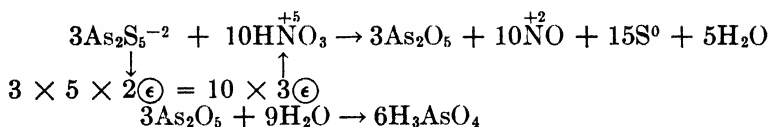
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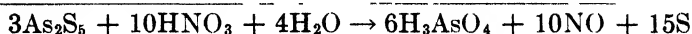
or



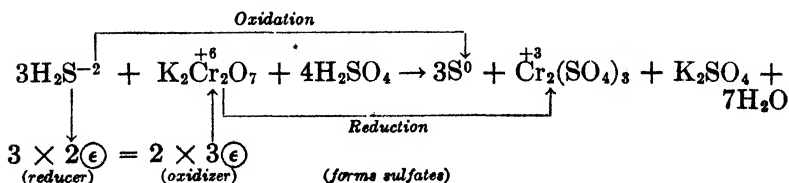
Likewise, the action of dilute nitric acid with arsenic sulfide will yield arsenic acid in addition to free sulfur and NO. The reaction follows in steps:



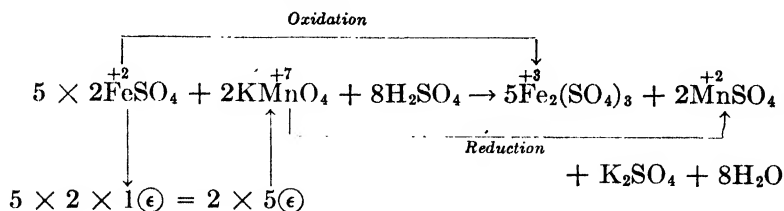
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The Reduction of Dichromates and Permanganates by Active Reducing Agents.—When hydrogen sulfide is passed into a solution of potassium dichromate containing an excess of sulfuric acid, it will be noted that the orange-red color of the dichromate ion, $\text{Cr}_2\text{O}_7^{-2}$, is changed to the green color of the chromic ion, Cr^{+3} , and also that free sulfur is formed simultaneously. That is, the sulfide ion, S^{-2} , in being converted to free sulfur, S^0 , loses 2 € (reducing agent). The chromium atoms in the $\text{Cr}_2\text{O}_7^{-2}$ ion go over to the chromic ion, Cr^{+3} , by the gain of 3 € per atom, or a total of 6 € for 2 chromium atoms (oxidizing agent). The complete molecular equation for this reaction is:

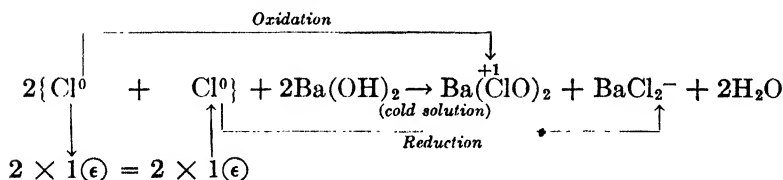


The oxidation of ferrous sulfate by potassium permanganate in a solution containing an excess of sulfuric acid follows:

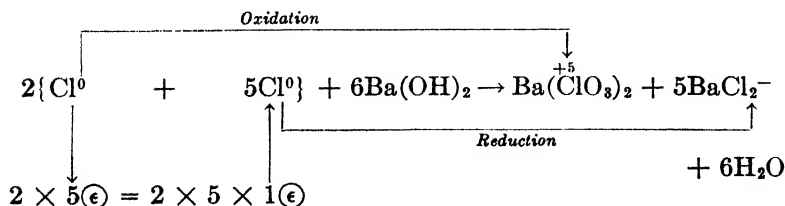


Note the mol ratio 10FeSO₄:2KMnO₄ or 5Fe²⁺:1MnO₄⁻

Example of Internal Oxidation and Reduction.—It is a well-known fact that when chlorine is passed into a cold solution of a base, a hypochlorite and a chloride are obtained. This represents a change in valence of (a) one chlorine atom from zero to +1 in the hypochlorite ion and (b) another chlorine atom from zero to -1 in the chloride ion. That is, chlorine is considered to be internally oxidized and reduced. This type of equation is illustrated by the following:



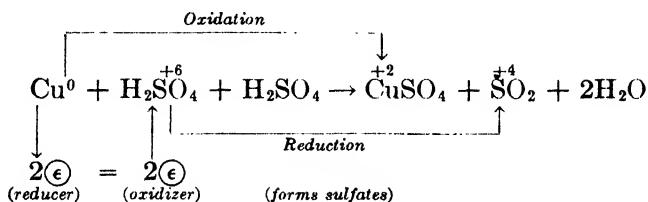
Likewise, if chlorine is passed into a hot solution of any base, a chlorate and a chloride are obtained. Thus,



A type problem is now undertaken that involves oxidation-reduction and also utilizes several principles presented in previous chapters.

Example.—Copper sulfate is prepared by treating metallic copper with hot concentrated sulfuric acid. Blue vitriol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is obtained by crystallization of copper sulfate from aqueous solution. (a) Calculate the number of gallons of sulfuric acid (sp. gr. = 1.835 and 93.2 per cent by weight of H_2SO_4) required to prepare 1 ton of blue vitriol. (b) How many cubic feet of SO_2 , measured at 75°F . and 29.8 in. of Hg, will be obtained by this reaction?

The chemical equation representing the foregoing reaction must be written



This equation tells us that

1 pound-mol of Cu requires 2 pound-mols of H_2SO_4 to form 1 pound-mol of CuSO_4 and 358.4 cu. ft. of SO_2 (S.T.P.).

Part (a). 1 pound-mol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ contains 1 pound-mol CuSO_4 .

249.71 lb. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ equals 1 pound-mol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

2,000 lb. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ equals $\frac{2,000}{249.71} = 8.01$ pound-mols of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, or 8.01 pound-mols of CuSO_4 .

To make 1 pound-mol of CuSO_4 requires 2 pound-mols of H_2SO_4 .

8.01 pound-mols of CuSO_4 requires $8.01 \times 2 = 16.02$ pound-mols of H_2SO_4 .

Since

1 pound-mol of $\text{H}_2\text{SO}_4 = 98.07$ lb. of H_2SO_4

16.02 pound-mols of $\text{H}_2\text{SO}_4 = 16.02 \times 98.07 = 1,571.08$ lb. of H_2SO_4

Now change 1,571.08 lb. of H_2SO_4 to gallons of sulfuric acid (sp. gr. = 1.835 and 93.2 per cent by weight of H_2SO_4) as follows:

The specific gravity of sulfuric acid = 1.835. This tells us that 1 gal. of sulfuric acid is 1.835 times as heavy as 1 gal. of water, or $1.835 \times 8.3 = 15.23$ lb. per gallon. But it is only 93.2 per cent pure H_2SO_4 ; then $15.23 \times 0.932 = 14.19$ lb. of active H_2SO_4 per gallon.

Since 14.19 lb. of H_2SO_4 is contained in 1 gal. of sulfuric acid, 1,571.08 lb. of H_2SO_4 will be contained in $1,571.08/14.19 = 110.71$ gal. of sulfuric acid (sp. gr. 1.835 and 93.2 per cent by weight of H_2SO_4) which will be required to make 1 ton of blue vitriol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Part (b). In preparing copper sulfate, the equation tells us that for every 1 pound-mol of CuSO_4 , 358.4 cu. ft. of SO_2 (S.T.P.) is formed at the same time.

From part (a), 2,000 lb. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ equals 8.01 pound-mols of CuSO_4 .

Then with 8.01 pound-mols of CuSO_4 , $8.01 \times 358.4 = 2,870.78$ cu. ft. of SO_2 (S.T.P.) will be formed.

It is now necessary to convert 2,870.78 cu. ft. of SO_2 at 32°F. and 29.92 in. of Hg (S.T.P.) to 75°F. and 29.8 in. Hg.

$$32^\circ\text{F.} = 32 + 460 = 492^\circ\text{R.}$$

$$75^\circ\text{F.} = 75 + 460 = 535^\circ\text{R.}$$

$$V \quad T \quad P$$

$$2,870.78 \times \frac{535}{492} \times \frac{29.92}{29.8} = 3,133.02 \text{ cu. ft. of } \text{SO}_2 \text{ at } 75^\circ\text{F. and}$$

29.8 in. of Hg.

Problems

Each of the following problems involves an oxidation-reduction reaction. Before attempting to solve any of these problems the complete and balanced equation is first drawn up for the reaction. The changes in valence numbers and the electron balance should also be indicated.

460. A sample of silver weighing 10 g. is dissolved in nitric acid, which has a specific gravity of 1.26 and contains 41.34 per cent by weight of HNO_3 . Calculate (a) the number of cubic centimeters of nitric acid necessary to dissolve the Ag. (b) How many cubic centimeters of nitric acid is used for oxidizing purposes? *Ans.* (a) 14.95 cc.

461. Calculate the volume of chlorine, at S.T.P., obtained by the interaction of 25 g. of lead dioxide and excess concentrated hydrochloric acid. *Ans.* 2.34 l.

462. Calculate the volume of chlorine, at standard conditions, liberated by the action of excess KMnO_4 with 100 cc. of hydrochloric acid, which

- has a specific gravity of 1.2 and contains 39.8 per cent by weight of HCl. *Ans.* 9.169 l.
463. Calculate the volume of H_2S , at standard conditions, required to reduce 1 g. of $\text{K}_2\text{Cr}_2\text{O}_7$ to chromic chloride, in a solution acidified with hydrochloric acid. *Ans.* 228 cc.
464. (a) How many cubic centimeters of sulfuric acid (sp. gr. 1.8439 and containing 97.5 per cent by weight of H_2SO_4) will be necessary to produce 2 l. of SO_2 , at standard conditions, by heating with copper turnings? (b) If the resultant solution is evaporated to dryness, what weight of crystalline $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ could be obtained from the residue? *Ans.* (a) 9.73 cc.; (b) 22.28 g.
465. A sample of brass (70 per cent Cu and 30 per cent Zn) weighing 5 g. is dissolved by nitric acid which has a specific gravity of 1.2 and contains 33.0 per cent by weight of HNO_3 . Calculate the number of cubic centimeters of this nitric acid solution required to dissolve the brass. *Ans.* 32.10 cc.
466. Calculate (a) the weight of sodium hypochlorite obtained by passing excess chlorine into a cold solution of caustic soda containing 100 g. of NaOH; (b) the volume of chlorine, at standard conditions, required to convert the NaOH to NaClO. *Ans.* (a) 93.05 g.; (b) 27.99 l.
467. Chlorine is passed into a hot solution of caustic potash, thus forming potassium chlorate. Calculate the weight of potassium chlorate formed by action of excess chlorine on a solution that contains 50 g. of KOH. *Ans.* 18.20 g.
468. Chlorine is passed into a hot solution of barium hydroxide which contains 30 g. of $\text{Ba}(\text{OH})_2$ in 1 l. of solution. Calculate (a) the volume of chlorine, at standard conditions, required for the complete reaction; (b) the weight of barium chlorate obtained as a product of this reaction. *Ans.* (a) 3.921 l.; (b) 8.87 g.
469. The use of thermite in the welding of steel depends on the reducing action of powdered aluminum on iron oxides (Goldschmidt process). "Red thermite" is a mixture of Al powder and Fe_2O_3 . "Black thermite" is a mixture of Al powder and Fe_3O_4 . Calculate the theoretical ratio by weight of (a) Al to Fe_2O_3 and (b) Al to Fe_3O_4 in each mixture when these substances undergo complete chemical action. *Ans.* (a) 1: 2.947; (b) 1: 3.219.
470. When an aqueous solution of sodium chloride is electrolyzed, chlorine is evolved at the anode and hydrogen at the cathode, and sodium hydroxide is also formed. Calculate (a) the volume, at S.T.P., of chlorine and hydrogen that can be obtained from 100 tons of sodium chloride, 99.6 per cent NaCl; (b) the weight of sodium hydroxide, 85 per cent NaOH, that could also be obtained. *Ans.* (a) 610,000 cu. ft. H_2 , 610,000 cu. ft. Cl_2 ; (b) 80.1 tons.
471. Calculate (a) the weight of $\text{K}_2\text{Cr}_2\text{O}_7$ required to react completely with 20 cc. of hydriodic acid (sp. gr. 1.7 and containing 57 per cent by weight of HI); (b) the weight of sublimed iodine obtained from this reaction. *Ans.* (a) 3.18 g.; (b) 8.24 g.

- 472.** A solution containing 10 g. of ferrous sulfate is treated with the requisite amounts of KMnO_4 and H_2SO_4 for complete chemical action. Calculate the weight of ferric sulfate obtained by this reaction. *Ans.* 13.17 g.
- 473.** A solution containing 20 g. of ferrous sulfate acidified with sulfuric acid is treated with excess nitric acid. Calculate (a) the weight of ferric sulfate produced in the reaction; (b) the volume of NO liberated at standard conditions. *Ans.* (a) 26.35 g.; (b) 985 cc.
- 474.** A quantity of sodium oxalate weighing 0.20 g. is dissolved in water and acidified with sulfuric acid. It was found that 30 cc. of a potassium permanganate solution were required for complete action. Calculate the weight of KMnO_4 that must have been present in the 30 cc. of solution. *Ans.* 0.0943 g.

Problems Involving Oxidation-reduction Reactions, without Answers, for Quizzes

- 475.** Calculate the volume of hydrogen sulfide, at 21°C . and 750 mm. pressure, that will be required to reduce 15 g. of ferric chloride to ferrous chloride.
- 476.** What volume of chlorine collected at 23°C . and 758 mm. pressure can be obtained from the interaction of 10 g. of $\text{K}_2\text{Cr}_2\text{O}_7$ and excess concentrated hydrochloric acid?
- 477.** Calculate the weight of coke, 97.5 per cent C, that will be necessary to produce 1,000 lb. of phosphorus by its action with calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, and sand, SiO_2 , in an electric furnace.
- 478.** Calculate the volume of phosphine, at standard conditions, produced by the heating of excess KOH solution with 25 g. of yellow phosphorus.
- 479.** A solution containing 0.83 g. of KI is acidified with dilute sulfuric acid. Calculate (a) the weight of ferric sulfate required to oxidize the iodide to free iodine; (b) the weight of iodine liberated.
- 480.** Iodide ion will reduce concentrated sulfuric acid to H_2S . A solution containing 0.52 g. of NaI is treated with excess concentrated sulfuric acid (sp. gr. 1.835 and containing 93.19 per cent by weight of H_2SO_4). Calculate (a) the weight of iodine produced by this action; (b) the number of cubic centimeters of sulfuric acid required for complete chemical action.
- 481.** A mixture of KCl and KMnO_4 is treated with concentrated sulfuric acid. Calculate (a) the weight of KMnO_4 required to oxidize 10 g. of KCl; (b) the volume of chlorine produced at standard conditions.
- 482.** A laboratory method for making bromine consists of treating a mixture of NaBr and $\text{K}_2\text{Cr}_2\text{O}_7$ with concentrated sulfuric acid. Determine the weights of (a) NaBr and (b) $\text{K}_2\text{Cr}_2\text{O}_7$ required to obtain 100 cc. of bromine (sp. gr. 3.119).
- 483.** When manganese dioxide, MnO_2 , is fused with K_2CO_3 and KClO_3 , a green mass is obtained containing potassium manganate, K_2MnO_4 . Determine the theoretical quantities of K_2CO_3 and KClO_3 required to react completely with 1 g. of MnO_2 .

484. What volume of hydrogen sulfide, at 25°C. and 750 mm. pressure, will be required to bring about the reduction of 10 g. of KMnO_4 in a solution acidified with sulfuric acid?
485. What volume of hydrogen sulfide, at 22°C. and 755 mm. pressure, will be required to reduce 10 g. of ferric sulfate in a solution acidified with sulfuric acid?
486. In the presence of a strong oxidizing agent, hydrogen peroxide can act as a reducing agent ($\text{H}_2\text{O}_2 - 2\text{e}^- \rightleftharpoons \text{O}_2 + 2\text{H}^+$). Calculate the number of cubic centimeters of hydrogen peroxide (sp. gr. 1.15 and containing 30 per cent by weight of H_2O_2) that will react completely with 10 g. of silver oxide.
487. Nitrous acid is oxidized to NO_3^- ion by MnO_4^- ion in an acid solution. (Hint: $\text{HNO}_2 + \text{H}_2\text{O} - 2\text{e}^- \rightleftharpoons \text{NO}_3^- + 3\text{H}^+$.) Calculate the weight of nitrous acid that will be oxidized by 5 g. of KMnO_4 in a solution containing sulfuric acid.
488. Calculate the weights of NH_4Cl and NaNO_3 that will be required to yield sufficient nitrous oxide to fill a steel cylinder of 2 cu. ft. capacity at 15°C. and produce in it a gas pressure of 146.97 lb. per square inch.
- Hint: $(2\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- \rightleftharpoons \text{N}_2\text{O} + 5\text{H}_2\text{O})$
 $(2\text{NH}_4^+ + \text{H}_2\text{O} - 8\text{e}^- \rightleftharpoons \text{N}_2\text{O} + 10\text{H}^+)$
489. A steel cylinder contains 250 gal. of nitrous oxide which weighs 3 lb. $14\frac{1}{2}$ oz. How much ammonium nitrate will be required to produce enough nitrous oxide, at standard conditions, to fill 10 cylinders of the foregoing capacity?
490. Calculate the volume of chlorine, collected at 20°C. and 755 mm. pressure, that is obtained by the interaction of 500 cc. of hydrochloric acid solution (sp. gr. 1.2 and containing 39.11 per cent by weight of HCl) and excess potassium dichromate.
491. Calculate the volume in cubic feet of chlorine, at 25°C. and 750 mm. pressure, necessary to yield 100 lb. of potassium chlorate by interaction with a hot solution of potassium hydroxide in excess.
492. (a) How many cubic centimeters of nitric acid (sp. gr. 1.20 and containing 32.31 per cent by weight of HNO_3) will be required to interact completely with 10 g. of phosphorus? (b) How many grams of phosphoric acid will be produced by this reaction?
493. Steam is passed over 100 g. of red-hot iron. Calculate (a) the weight of magnetic oxide of iron, Fe_3O_4 , produced; (b) the volume of hydrogen evolved at 0°C. and 760 mm. pressure.
494. (a) How many cubic centimeters of nitric acid (sp. gr. 1.20 and containing 32.31 per cent by weight of HNO_3) will be required to interact completely with 100 g. of iodine? (b) How many grams of iodic acid will be produced by this reaction?
495. Manganese dioxide is treated with an excess of concentrated hydrochloric acid. The chlorine liberated by this action is absorbed in cold KOH solution. Calculate the amount of MnO_2 required to prepare 100 g. of potassium hypochlorite.

- 496.** Lead dioxide is treated with an excess of concentrated hydrochloric acid. The chlorine liberated by this action is absorbed in hot KOH solution. Calculate the amount of PbO_2 required in the preparation of 100 lb. of potassium chlorate.
- 497.** Calculate (a) the number of cubic centimeters of nitric acid (sp. gr. 1.41 and containing 67.50 per cent by weight of HNO_3) that will react completely with 10 g. of metallic Cu. (b) What volume of NO_2 , collected at 23°C . and 745 mm. pressure, will be liberated by this action?
- 498.** A dime (weight 2.488 g., contains Ag 92.5 per cent; Cu 7.5 per cent) is dissolved in nitric acid which has a specific gravity of 1.225 and contains 40.58 per cent by weight of HNO_3 . Calculate the actual number of cubic centimeters of acid that will be required to dissolve the dime completely.
- 499.** A quantity of sodium oxalate weighing 0.1970 g. is dissolved in water, and a slight excess of sulfuric acid is added. It was found that 30.7 cc. of potassium permanganate solution completely oxidized the foregoing amount of $\text{Na}_2\text{C}_2\text{O}_4$. Calculate the weight of KMnO_4 in each cubic centimeter of solution.
- 500.** To destroy the poison-ivy plant, it is recommended that calcium chlorate, $\text{Ca}(\text{ClO}_3)_2$, be used in a concentration of $\frac{1}{2}$ lb. per gallon. What volume (cubic feet) of chlorine, measured at 70°F . and 30 in. Hg, passed into a hot $\text{Ca}(\text{OH})_2$ solution will be required to make 100 gal. of calcium chlorate solution of the foregoing strength?

CHAPTER IX

OUTLINE

32.685 g. of Zn = chemically 8.99 g. of Al = 23.00 g. of Na = 27.92 g. of Fe, for each of these quantities will liberate the same weight of hydrogen (1.008 g.) from acids. These weights are chemically equivalent.

In water each 8 g. of oxygen is united with 1.008 g. of hydrogen. Therefore, 8 g. of oxygen is equal chemically to 1.008 g. of hydrogen.

Eight parts by weight of oxygen is used as the basis of combining weights. That weight of an element which combines with 8 parts by weight of oxygen is the combining weight of the element.

Chemical equivalents of compounds.

Examples. Chemical equivalents of (a) an acid, (b) a base, (c) a salt, (d) an oxidizing agent.

Molar and normal solutions.

Standard solution. A solution whose strength is accurately known.

COMBINING WEIGHTS—CHEMICAL EQUIVALENTS

Most of us have observed in the laboratory that many of the metals dissolve in acids and that hydrogen is liberated when they dissolve. By dissolving weighed amounts of the various metals in acids and measuring the hydrogen evolved and reduced to standard conditions, it has been found, for example, that

32.685 g. of zinc liberates 1.008 g. of hydrogen, at 0°C., 760 mm.
8.99 g. of aluminum liberates 1.008 g. of hydrogen, at 0°C.,
760 mm.

23.00 g. of sodium liberates 1.008 g. of hydrogen, at 0°C., 760 mm.
27.92 g. of iron liberates 1.008 g. of hydrogen, at 0°C., 760 mm.

We see that to liberate 1.008 g. of hydrogen from acids, 32.68 g. of zinc is necessary; or if we used sodium instead of zinc, 23.00 g. of sodium would be necessary. We would decide from this that 32.68 g. of zinc is equivalent in its chemical action to 23.00 g. of sodium. Likewise, we should need 8.99 g. of aluminum or 27.92 g. of iron to liberate 1.008 g. of hydrogen; 8.99 is the number of grams of aluminum that is equivalent in its chemical action to 27.92 g. of iron or to 32.68 g. of zinc or to 23.00 g. of sodium.

or to 1.008 g. of hydrogen. These weights of these elements are equivalent to each other chemically.

If we pass an electric current through water acidified with sulfuric acid, the water is split up into hydrogen and oxygen, the elements that compose it. The hydrogen collects at the cathode; the oxygen, at the anode. If we measure the volume and determine the weight of the quantity of gas evolved at each electrode, we find that for each 1.008 g. of hydrogen, which collects at the cathode, 8 g. of oxygen collects at the anode. We decide at once that in water each 1.008 g. of hydrogen is united with 8 g. of oxygen. This is the proportion in which they combine; 8 g. of oxygen is, therefore, chemically equivalent to 1.008 g. of hydrogen, also

32.685 g. of Zn \approx 1.008 g. hydrogen \approx 8 g. oxygen

8.99 g. of Al \approx 1.008 g. hydrogen \approx 8 g. oxygen

23.000 g. of Na \approx 1.008 g. hydrogen \approx 8 g. oxygen

27.920 g. of Fe \approx 1.008 g. hydrogen \approx 8 g. oxygen

We should expect, then, if Zn or Al or Na or Fe combined with oxygen, that they would combine in the proportions

32.685 g. of Zn with 8 g. of oxygen

8.99 g. of Al with 8 g. of oxygen

23.000 g. of Na with 8 g. of oxygen

27.920 g. of Fe with 8 g. of oxygen

The results of repeated analyses confirm our expectations and show them to be true.

These various weights of Zn, Al, Na, and Fe are called **combining weights**, or **gram-equivalents**, of these elements.

We can define the combining weight, or gram-equivalent, of an element as that *quantity of the element which reacts with or replaces 1 gram-atom of hydrogen (1.008 g.) or combines with $\frac{1}{2}$ gram-atom of oxygen (8 g.)*.

There is a direct relationship between the gram-atomic weight of an element and its gram-equivalent. Thus:

$$\frac{1 \text{ gram-atom of H}}{1 \text{ gram-equivalent of H}} = \frac{1.008 \text{ g.}}{1.008 \text{ g.}} = \frac{1}{1}$$

and

$$\frac{1 \text{ gram-atom of O}}{1 \text{ gram-equivalent of O}} = \frac{16.00 \text{ g.}}{8.00 \text{ g.}} = 2$$

and

$$\frac{1 \text{ gram-atom of Al}}{1 \text{ gram-equivalent of Al}} = \frac{26.97 \text{ g.}}{8.99 \text{ g.}} = 3$$

and

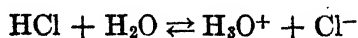
$$\frac{1 \text{ gram-atom of Zn}}{1 \text{ gram-equivalent of Zn}} = \frac{65.39 \text{ g.}}{32.69 \text{ g.}} = 2$$

The numerators 1, 2, 3, and 2 for H, O, Al, and Zn, respectively, are, in reality, the valence numbers of these elements. This justifies the statement that the *gram-equivalent of an element is equal to the gram-atomic weight of that element divided by its valence number*.

Chemical Equivalents of Compounds.—The principle of combining weights, or chemical equivalents, may be extended to compounds. The term *chemical equivalent* will be used in this book when referring to compounds; the term *combining weight*, when referring to elements.

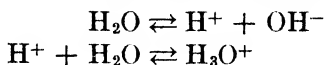
The Theory of Electrolytic Dissociation postulates that, when electrolytes are dissolved in water, their molecules dissociate into two or more electrically charged particles, called ions. It is a well-known fact that all acids, in aqueous solution, yield hydrogen ions, H^+ , and that all bases yield hydroxyl ions, OH^- ; in fact, these ions are the principal constituents of these classes of compounds and respectively give to them their characteristic properties. When an acid is neutralized by a base, the reaction is, in reality, a union of the H^+ ions of the acid with the OH^- ions of the base to form the very slightly ionized $H(OH)$ molecule.

In Chap. III it was stated that the hydrogen ion, H^+ , is a proton (unit positive charge). Since an acid dissociates into H^+ (proton) and a negative ion (anion), it can be said that an acid is a donor of protons. On the other hand, a base is a proton acceptor. This is in accordance with the Brönsted theory of acids and bases. When hydrogen chloride is dissolved in water we obtain a solution of hydrochloric acid, as shown by the following equation:

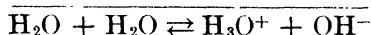


We note that the proton (H^+) donated by the acid is accepted by water (which becomes a base) to form the positively charged H_3O^+ , called the hydronium ion.

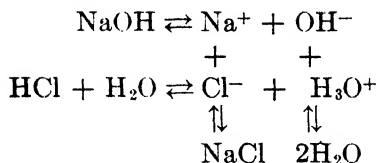
The ionization of pure water can be represented by



or



Thus, water acts both as an acid and as a base, since there are present, to a slight extent, hydronium ions and hydroxyl ions. In aqueous solutions, then, we have H_3O^+ instead of hydrogen ions, H^+ (protons). The acidic properties depend on the presence of the hydronium ion, and the basic properties depend on the hydroxyl ion, OH^- . The neutralization of sodium hydroxide solution with hydrochloric acid can be represented by the following ionic equations:



The reaction is really one in which $\text{H}_3\text{O}^+ + \text{OH}^-$ forms $2\text{H}_2\text{O}$. In inorganic chemistry, most of our chemical reactions take place in aqueous solutions, and the H^+ is used synonymously with H_3O^+ and will be so used throughout this text. Then $1\text{H}^+ \approx 1\text{H}_3\text{O}^+ \approx 1\text{OH}^-$, and 1.008 g. of $\text{H}^+ \approx 17.008$ g. of $\text{OH}^- \approx 8$ g. of O.

(a) *Gram-equivalents of Acids.*—Since all acids contain the replaceable hydrogen ion (proton), we can define the gram-equivalent of an acid as that quantity of acid which contains 1.008 g., or 1 gram-atom, of replaceable hydrogen. Thus, 1 gram-mol, or 36.465 g., of HCl contains 1 gram-atom of hydrogen. Therefore, the gram equivalent of $\text{HCl} = 36.465$ g. of HCl. Or 1 gram-equivalent of HCl contains 1 gram-atom of hydrogen. In the case of sulfuric acid there are

2 gram-atoms of H in 1 gram-mol, or 98.076 g., of H_2SO_4 .

1 gram-atom of H in $\frac{1}{2}$ gram-mol, or 49.038 g., of H_2SO_4 .

Therefore, 1 gram-equivalent of H_2SO_4 is 49.038 g. of H_2SO_4 . Likewise, 1 gram-equivalent of H_3PO_4 is $\frac{1}{3}$ gram-mol, or $98.004/3$ g. = 32.668 g., of H_3PO_4 .

(b) *Gram-equivalents of Bases.*—All bases contain the OH^- ion, and we have learned that the gram-equivalent of the hydroxyl radical, OH^- , is 17.008 g. of OH^- which is chemically equivalent to 1.008 g. of H^+ . The gram-equivalent of a base is defined as that quantity which contains 17.008 g. of OH^- , or 1 gram-equivalent of OH^- . Thus, 1 gram-equivalent of OH^- is contained in 1 gram-mol, or 40.005 g., of NaOH . Therefore, 1 gram-equivalent of NaOH is 40.005 g. of NaOH .

Consider ferric hydroxide, $\text{Fe}(\text{OH})_3$:

There are 3 gram-equivalents of OH^- in 1 gram-mol of $\text{Fe}(\text{OH})_3$, or 106.864 g. of $\text{Fe}(\text{OH})_3$. Then, 1 gram-equivalent of OH^- is contained in $\frac{1}{3}$ gram-mol of $\text{Fe}(\text{OH})_3$, or $106.864/3$ g. = 35.62 g. of $\text{Fe}(\text{OH})_3$.

Therefore, 35.62 g. of $\text{Fe}(\text{OH})_3$ is 1 gram-equivalent of $\text{Fe}(\text{OH})_3$.

(c) *Gram-equivalents of Salts.*—Salts are formed by the replacement of the hydrogen of an acid by a metallic ion. The gram-equivalent of a salt may be defined as that quantity of the salt that contains 1 gram-equivalent of the metallic ion. To be sure, 1 gram-equivalent of a metallic ion is chemically equivalent to 1 gram-atom of hydrogen. Thus 1 gram-mol of NaCl contains 1 gram-equivalent of Na which is chemically equivalent to 1 gram-atom of H , or 58.454 g. of $\text{NaCl} \approx 1.008$ g. of hydrogen. Therefore, 1 gram-equivalent of NaCl = 58.454 g. of NaCl .

Consider sodium carbonate, Na_2CO_3 :

2 gram-equivalents of Na are contained in 1 gram-mol of Na_2CO_3 . 1 gram-equivalent of Na is contained in $\frac{1}{2}$ gram-mol of Na_2CO_3 , or $105.994/2 = 52.997$ g. of Na_2CO_3 .

Therefore, 1 gram-equivalent of $\text{Na}_2\text{CO}_3 = 52.997$ g. of Na_2CO_3 .

In the case of chromic sulfate, $\text{Cr}_2(\text{SO}_4)_3$: The valence number of chromium is +3. That is, each Cr atom is capable of replacing 3 H^+ , or 1 gram-atom of Cr reacts with 3 gram-atoms of H^+ , and 2 gram-atoms of Cr will react with 6 gram-atoms of H^+ , or $\frac{2}{6}$ or $\frac{1}{3}$ gram-atom of Cr will react with 1 gram-atom

of H^+ . The gram-equivalent of Cr will then be $\frac{1}{3}$ gram-atom of Cr, or $52.01/3$ g. = 17.33 g. of Cr.

In $Cr_2(SO_4)_3$ there are 6 gram-equivalents of Cr in 1 gram-mol of $Cr_2(SO_4)_3$, or 1 gram-equivalent of Cr in $\frac{1}{6}$ gram-mol, or $392.18/6$ g. = 65.36 g. of $Cr_2(SO_4)_3$. Therefore 1 gram-equivalent of $Cr_2(SO_4)_3$ is 65.36 g. of $Cr_2(SO_4)_3$.

It is to be noted that a direct relationship exists between the gram-molecular weight and the gram-equivalent weight for the various compounds, as in the case of elements. Using NaCl, Na_2CO_3 , and $Cr_2(SO_4)_3$ as examples, these ratios can be expressed as follows:

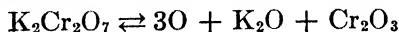
$$\begin{array}{rcl} \frac{1 \text{ gram-mol NaCl}}{1 \text{ gram-equivalent NaCl}} & = \frac{58.454 \text{ g.}}{58.454 \text{ g.}} & = 1 \\ \frac{1 \text{ gram-mol Na}_2\text{CO}_3}{1 \text{ gram-equivalent Na}_2\text{CO}_3} & = \frac{105.994 \text{ g.}}{52.997 \text{ g.}} & = 2 \\ \frac{1 \text{ gram-mol Cr}_2(\text{SO}_4)_3}{1 \text{ gram-equivalent Cr}_2(\text{SO}_4)_3} & = \frac{392.18 \text{ g.}}{65.36 \text{ g.}} & = 6 \end{array}$$

The numerators 1, 2, and 6 are actually equal to the total positive polar valence of the metallic ions in each of these compounds. A simple rule to follow in order to determine the gram-equivalent of a compound is to divide the gram-molecular weight of the compound by its total positive polar valence. This rule applies only to acids, bases, and salts.

(d) *Method A for Gram-equivalents of Oxidizing Agents.*—The weight of the oxidizing agent that will liberate 8.0 g. of oxygen is the gram-equivalent of the substance when acting as an oxidizer.

Example.—Calculate the chemical equivalent of $K_2Cr_2O_7$ as an oxidizing agent in an acid solution.

When $K_2Cr_2O_7$ acts as an oxidizing agent, 1 molecule of it gives 3 atoms of oxygen, as indicated by the equation



1 gram-mol, or 294.2 g., of $K_2Cr_2O_7$ furnishes 3×16.0 , or 48.0 g., of oxygen.

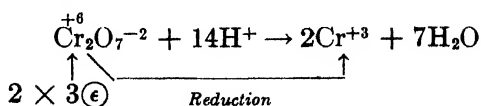
8.0 g. of O is one-sixth of 48.0 g. of oxygen. The gram-equivalent of $K_2Cr_2O_7$ is, therefore, one-sixth of the molecular weight, or $\frac{1}{6} \times 294.2$ g. = 49.033 g.

Method B for Gram-equivalents of Oxidizing and Reducing Agents.—As stated in Chap. VIII, oxidizers are substances that contain an atom or ion capable of receiving or gaining electrons. Substances that contain an atom or ion capable of giving up or furnishing electrons are called reducers. It should be noted that in all oxidation and reduction reactions there is a change in valence numbers of certain atoms. That is, in the case of the oxidizing agents the valence number of the atom or ion that gains electrons is algebraically decreased. In the case of reducing agents, the valence number of the atom or ion that gives up electrons is algebraically increased. The information is readily obtainable at a glance from Table X, which contains the common oxidizers and reducers generally met with in oxidation-reduction reactions.

Since all these changes in valence numbers of various atoms or ions in oxidizers and reducers involve a gain and loss of electrons, respectively, it is evident that the gram-equivalent is related to the number of electrons transferred. In the case of oxidizers, the *gram-equivalent is obtained by dividing the total gram-molecular weight of the oxidizer by the total number of electrons gained by the substance (or the total numerical or algebraic change in valence numbers)* when it is reduced. Also, the gram-equivalent of a reducer is obtained by dividing the total gram-molecular weight of the reducer by the total number of electrons given up by the substance (or the total algebraic change in valence numbers) when it is oxidized.

Example.—Determine the gram-equivalent of $K_2Cr_2O_7$ as an oxidizer in an acid medium.

The oxidizing effects of $K_2Cr_2O_7$ in an acid solution are due to the fact that the dichromate ion, $Cr_2O_7^{-2}$, in the presence of H^+ is reduced to the chromic ion, Cr^{+3} . This is accomplished by a gain of 3ϵ per atom of Cr in the dichromate ion, or a change of 3 in the valence number of each Cr atom, or a total of 6 for the 2 Cr atoms in the dichromate ion. This can be represented by



Note that the total change in valence number of the Cr atom is 6,

or a total gain of 6€ is involved. It follows that the gram-equivalent of $\text{K}_2\text{Cr}_2\text{O}_7$ is readily obtained by dividing the total gram-molecular weight by 6, or $294.20/6 \text{ g.} = 49.033 \text{ g.}$ of $\text{K}_2\text{Cr}_2\text{O}_7 = \text{gram-equivalent of } \text{K}_2\text{Cr}_2\text{O}_7$. The gram-equivalents of reducers are obtained in the same way.

Just as we have gram-equivalents, it is conceivable that we could have ounce-equivalents, pound-equivalents, kilogram-equivalents, and so on. There are occasions in industrial calculations when it is convenient to use the pound-equivalent; and of course the chemical equivalent of the substance would have the same significance in the larger as in the smaller scale units. (Why?)

CONCENTRATION—MOLAR AND NORMAL SOLUTIONS

In dealing with solutions of various substances it is, generally, very necessary to know the quantitative relationship existing between the solute (dissolved substance) and the solvent—in other words, to know the concentration of the solution. Of the several ways of expressing concentration of solutions the following are useful: (a) grams of solute per liter of solution (g./l.), *i.e.*, volume concentration; (b) grams of solute per 1,000 g. of solvent, *i.e.*, weight concentration; (c) the quantity unit of 1 gram-mol of substance in 1,000 cc. of solution; (d) the quantity unit of one gram-equivalent of substance in 1,000 cc. of solution.

A solution that contains 1 gram-mol of solute in 1,000 cc. of solution is called a **molar solution**. The molar solution is symbolized by M , or the unit of gram-mols per liter is symbolized by **m./l.** Thus a molar solution of sodium carbonate would contain 1 gram-mol, or 105.994 g., of Na_2CO_3 per liter of solution and would be represented as $M \text{ Na}_2\text{CO}_3$. A $2 M \text{ Na}_2\text{CO}_3$ solution would, obviously, contain 2 gram-mols of Na_2CO_3 , or $2 \times 105.994 \text{ g.} = 211.988 \text{ g.}$ of Na_2CO_3 per liter of solution. We then say that the *molarity* of this solution is $2 M$ in Na_2CO_3 .

Example 1.—The solubility of silver chloride is $1.80 \times 10^{-3} \text{ g./l.}$ What is the molarity of this solution?

$$1 \text{ gram-mol of } \text{AgCl} = 143.337 \text{ g. of } \text{AgCl}$$

143.337 g./l. of AgCl represents a concentration of 1 m./l. of AgCl .

1 g. per liter of AgCl represents a concentration of $1/143.337$ m./l. of AgCl.

1.80×10^{-3} g./l. of AgCl represents a concentration of $1.80 \times 10^{-3}/143.337$ m./l. = 1.25×10^{-5} m./l. of AgCl = molarity.

Example 2.—The solubility of magnesium carbonate is 2.7×10^{-3} m./l. How many grams of MgCO_3 is contained in 100 cc. of this solution?

1 m./l. of MgCO_3 (M MgCO_3) contains 1 gram-mol per liter, or 84.33 g./l. of MgCO_3 .

2.7×10^{-3} m./l. of MgCO_3 would contain $(2.7 \times 10^{-3}) \times 84.33$ g./l. = 0.227 g./l. or 0.0227 g. per 100 cc. of solution.

Example 3.—A solution contains 5 cc. of hydrochloric acid (sp. gr. 1.20 and 39 per cent by weight of HCl) in 100 cc. What is the molarity of this solution?

The hydrochloric acid contains $1.20 \times 0.39 = 0.468$ g. of HCl in 1 cc.

5 cc. of this hydrochloric acid would contain 5×0.468 g. = 2.34 g. of active HCl. Then 2.34 g. of HCl would be contained in 100 cc. of this acid solution, or 23.4 g. of HCl per liter.

A molar solution of hydrochloric acid contains 36.465 g. of HCl per liter, or 36.465 g./l. of HCl represents a concentration of 1 m./l. of HCl. 23.4 g./l. of HCl would represent a concentration of $23.4/36.465$ m./l. = 0.64 m./l. of HCl, or 0.64 M HCl = molarity.

Example 4.—What is the molarity of concentrated sulfuric acid (sp. gr. 1.835 and 93.56 per cent by weight of H_2SO_4)?

This sulfuric acid contains $1.835 \times 0.9356 = 1.7168$ g. of H_2SO_4 per cubic centimeter or 1,716.8 g./l.

98.076 g./l. of H_2SO_4 represents a concentration of 1 m./l. of H_2SO_4 .

1,716.8 g./l. of H_2SO_4 would represent a concentration of $1,716.8/98.076$ m./l. = 18.5 m./l., or 18.5 M H_2SO_4 = molarity.

NORMAL SOLUTIONS

It has been found especially convenient and useful in volumetric chemical analysis to make up standard solutions in which the number of grams of the substance dissolved in each liter of sol . .

tion is the same numerically as the **chemical equivalent** of that compound. Such solutions are called *normal solutions* and are frequently designated by the letter *N*. It will be recalled that in developing our knowledge of chemical equivalents we decided to consider the chemical equivalent of a compound as that weight of it which is equal chemically to 8 g. of oxygen or to 1.008 g. of hydrogen. Therefore, a **normal solution of any substance is one that contains in each 1,000 cc. of solution that weight of the substance which is equivalent to 8 g. of oxygen, or to 1.008 g. of hydrogen.**

Stated in another manner, a **normal solution is one that contains 1 gram-equivalent of the substance dissolved in 1 l., or 1,000 cc., of solution.**

On the basis of 1 cc. as unit volume, a normal solution would contain 1 gram-milliequivalent (the prefix milli- denotes one one-thousandth) of the substance in 1 cc. of solution, or, better still, 1 milligram-equivalent of the substance in 1 cc. of solution.

Example.—Determine the quantities of each of the following necessary to prepare a normal solution of each of these substances: (a) $(\text{NH}_4)_2\text{SO}_4$; (b) H_3PO_4 ; and (c) $\text{Ba}(\text{OH})_2$.

It is necessary only to determine the gram-equivalents of each of the three substances, and each of these quantities contained in 1 l. of solution will be the required amounts, respectively, for preparation of normal solutions. Thus:

(a) 1 gram-mol of $(\text{NH}_4)_2\text{SO}_4 = 132.14$ g. of $(\text{NH}_4)_2\text{SO}_4$.

1 gram-equivalent of $(\text{NH}_4)_2\text{SO}_4 = \frac{132.14}{2}$ g. = 66.07 g. of $(\text{NH}_4)_2\text{SO}_4$ (why?)

Then

66.07 g./l. = 0.06607 g./cc. = 66.07 mg./cc. = *N* $(\text{NH}_4)_2\text{SO}_4$

(b) 1 gram-mol of $\text{H}_3\text{PO}_4 = 98.004$ g. of H_3PO_4 .

1 gram-equivalent of $\text{H}_3\text{PO}_4 = \frac{98.044}{3}$ g. = 32.681 g. of H_3PO_4 (why?)

Then

32.681 g./l. = 0.032681 g./cc. = 32.681 mg./cc. = *N* H_3PO_4

(c) 1 gram-mol of $\text{Ba}(\text{OH})_2 = 171.376$ g. of $\text{Ba}(\text{OH})_2$.

$$1 \text{ gram-equivalent of Ba(OH)}_2 = \frac{171.376}{2} \text{ g.} = 85.688 \text{ g. of Ba(OH)}_2 \text{ (why?)}$$

Then

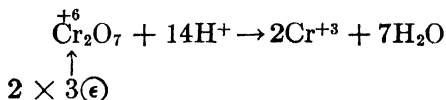
$$85.688 \text{ g./l.} = 0.085688 \text{ g./cc.} = 85.688 \text{ mg./cc.} = N \text{ Ba(OH)}_2$$

Since all normal solutions are all on the same basis, *i.e.*, based on 1 gram-equivalent of substance per liter of solution, we should expect that equal volumes of all normal solutions would be chemically equivalent. For instance, 1 cc. of *N* HCl will exactly neutralize 1 cc. of *N* Ba(OH)₂ or 1 cc. of any other *N* base. Also, 1 cc. of *N* AgNO₃ will react completely with 1 cc. of *N* NaCl to form 1 gram-milliequivalent or 1 milligram-equivalent of AgCl. These important relations are given more extensive consideration in Chap. X.

It has been shown (page 149) that to determine the gram-equivalents of oxidizers by using Method A, it is necessary to determine that quantity of oxidizer which will liberate 8 g. of oxygen in an oxidation-reduction reaction. This method has its objections, since not all oxidizers contain oxygen. By Method B, which can be applied generally to all oxidizers, the gram-equivalent is obtained by dividing the total gram-atomic weight or the gram-molecular weight of the oxidizer either by the total number of electrons gained by an atom or molecule of the oxidizer or by the total algebraic change in the valence number of an atom or ion of the oxidizer, when it is reduced.

Example.—Determine the quantity of K₂Cr₂O₇ necessary to make a normal solution of this substance when used as an oxidizer in an acid medium.

From the table of oxidizers and reducers we note the following:



Since 1 Cr₂O₇⁻² is associated with 2 K⁺ ions in the molecule of K₂Cr₂O₇, it is readily seen that the gram-equivalent of K₂Cr₂O₇ is obtained by dividing the total gram-molecular weight of the compound by the total number of electrons gained by the 2 Cr atoms in the Cr₂O₇⁻² ion or the total change in valence of Cr

when it is reduced. This amounts to 6 € for the 2 Cr atoms, each of which goes from +6 to +3. Then one-sixth of the gram-molecular weight of $K_2Cr_2O_7$, or $294.2/6$ g., or 49.033 g., is one gram-equivalent of $K_2Cr_2O_7$. To make 1 l. of a normal solution of $K_2Cr_2O_7$ when it is functioning as an oxidizing agent, it is necessary only to dissolve 49.033 g. of $K_2Cr_2O_7$ in sufficient distilled water to make 1 l. of the solution.

STANDARD SOLUTIONS

It should be emphasized that any solution whose concentration is known is called a **standard solution**. A solution made up arbitrarily for certain analytical processes may be considered as standard. However, solutions of definite molarity or definite normality come more closely within the category of truly standard solutions. The process of determining the actual strength (molarity or normality) is known as standardization. Methods of standardization are explained in quantitative chemical analysis textbooks, and no attempt is made to give the details of these methods in this book. The advantage of expressing concentrations in terms of normality will be apparent when one considers the fact that normal solutions have a common basis—the gram-equivalent weight per liter of solution—which, of course, makes equal volumes of all normal solutions exactly equivalent to each other.

NORMALITY

In the examples so far we have considered only one normal (1 *N*) solutions. In making up standard solutions it is usually impracticable to make up a solution exactly 1.0000 . . . *N*. For many purposes the procedure is to make up a solution stronger or weaker than a normal solution. In this event the concentration is expressed in terms of *normality*. To illustrate: A solution that contains in each liter one-tenth as much of a compound as is necessary to make a normal solution of that compound, or $\frac{1}{10}$ gram-equivalent of that compound, would, of course, have a normality of one-tenth that of a normal solution, or be a tenth normal solution (0.1 *N* solution). A solution that contains in each liter 0.5213 times as much of the compound as is necessary

to make a normal solution, or 0.5213 gram-equivalent of the compound, has a normality of 0.5213, or 0.5213 *N*.

Example.—Determine the weight of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ required to prepare 250 cc. of 0.525 *N* solution of this salt.

The chemical equivalent of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is one-half its molecular weight, or $246.492/2 = 123.246$. Then 123.246 g., or 1 gram-equivalent, of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in water and diluted to exactly 1,000 cc. will make a normal solution.

To make a solution of a normality equal to 0.525, or 0.525 *N*, we shall have to take 0.525×123.246 g., or 64.704 g., of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ per liter of solution. For 250 cc. of solution, the weight of the salt needed will be $250/1,000 \times 64.704 = 16.176$ g.

Problems

501. Calculate the combining weights of the metals in the following oxides: ZrO_2 , TiO_2 , UO_2 . *Ans.* 22.65; 12.02; 59.54.
502. Calculate the combining weight of the first element in each of the following: cobaltous oxide, lithium oxide, bismuth oxide, arsenious sulfide, boron nitride. *Ans.* 29.48; 6.94; 69.66; 24.98; 3.63.
503. Calculate the combining weights of iron in ferrous chloride and in ferric chloride; of copper in cuprous oxide and in cupric oxide. *Ans.* Fe, 27.92, 18.61; Cu, 63.57, 31.78.
504. Calculate the combining weights of arsenic in arsenic trichloride and in arsenic pentachloride; of chromium in chromic oxide and in chromium trioxide. *Ans.* As, 24.98, 14.99; Cr, 17.33, 8.66.
505. It is found that 15.2151 g. of silver combines with bromine to form 26.487 g. of silver bromide. The combining weight of Ag is 107.88. Calculate from these data the combining weight of bromine. *Ans.* 79.92.
506. By analysis 1.25 g. of ferric oxide was found to contain 0.8742 g. of Fe. Calculate the combining weight of iron from these data. *Ans.* 18.61.
507. Determine the chemical equivalent of KMnO_4 when this substance is used as an oxidizer in a solution acidified with sulfuric acid. *Ans.* 31.60.
508. Determine the chemical equivalent of dilute nitric acid when used (a) as an acid, (b) as an oxidizer. *Ans.* (a) 63.0; (b) 21.00.
509. Calculate the chemical equivalent of concentrated sulfuric acid when used (a) as an acid, (b) as an oxidizer. *Ans.* (a) 49.038; (b) 49.038.
510. Calculate the chemical equivalent of each of the following: (a) H_2F_2 , (b) $\text{Al}(\text{OH})_3$, (c) $\text{Ca}_3(\text{PO}_4)_2$, (d) La_2O_3 . *Ans.* (a) 20.008; (b) 25.998; (c) 51.71; (d) 54.3.

511. Calculate the chemical equivalent of each of the following: (a) KHCO_3 , (b) H_3BO_3 , (c) PH_3 , (d) V_2O_5 .
Ans. (a) 100.10; (b) 20.614; (c) 11.35; (d) 18.192.
512. Calculate the chemical equivalent of each of the following: (a) AsH_3 , (b) CuS , (c) KCN , (d) MoO_3 .
Ans. (a) 25.994; (b) 47.817; (c) 65.104; (d) 24.0.
513. Calculate the chemical equivalent of each of the following: (a) $\text{HC}_2\text{H}_3\text{O}_2$, (b) $\text{Ba}(\text{OH})_2$, (c) K_3PO_4 , (d) KClO .
Ans. (a) 60.03; (b) 85.69; (c) 70.78; (d) 90.56.
514. Calculate the chemical equivalent of each of the following: (a) $\text{H}_4\text{P}_2\text{O}_7$, (b) Cu_2SO_4 , (c) $\text{Na}_2\text{Cr}_2\text{O}_7$ as an oxidizer, (d) RbOH .
Ans. (a) 44.53; (b) 111.60; (c) 43.66; (d) 102.45.
515. Calculate the chemical equivalent of each of the following: (a) $\text{K}_4\text{Fe}(\text{CN})_6$, (b) $\text{Ba}_3(\text{PO}_3)_2$, (c) MnO_2 as an oxidizer, (d) CsOH .
Ans. (a) 92.06; (b) 95.03; (c) 43.46; (d) 149.81.
516. When 2.5 g. of Zn is dissolved by excess hydrochloric acid, 856.6 cc. of hydrogen is evolved, measured at standard conditions. Calculate the combining weight of Zn. *Ans.* 32.6.
517. When 1.25 g. of Al is acted upon by dilute sulfuric acid in excess, 1,549.8 cc. of hydrogen is evolved measured at standard conditions. Calculate the combining weight of aluminum. *Ans.* 9.03.
518. When steam is passed over 5 g. of red-hot iron, hydrogen is evolved which measures 2,674.3 cc. at standard conditions. Calculate the combining weight of Fe. *Ans.* 20.94.
519. By experiment it was found that 2.541 g. of Zn, dissolved by excess hydrochloric acid, yielded 963.66 cc. of hydrogen, collected over water, at 21°C . and 758 mm. pressure. From these data calculate the combining weight of Zn. Vapor pressure of water at 21°C . = 18.5 mm.
Ans. 32.7.
520. It was found that 2.5 g. of aluminum acted upon by a dilute solution of NaOH and heated evolved 3,393.6 cc. of hydrogen, collected over mercury at 20°C . and 745 mm. pressure. From these data calculate the combining weight of Al. *Ans.* 9.03.
521. To a solution of mercuric chloride, 5 g. of zinc was added. The zinc displaced 15.343 g. of Hg. The combining weight of Zn is 32.685. Calculate the combining weight of Hg. *Ans.* 100.3.
522. A piece of Zn is placed in a solution containing 1.8962 g. of SnCl_2 . After the action had ceased, the tin precipitated was found to weigh 1.187 g., and the Zn was found to have lost 0.6537 g. The combining weight of Zn is 32.685. From these data calculate the combining weights of tin and of chlorine. *Ans.* 59.34; 35.45.
523. A sample of Zn weighing 2.0226 g. was treated with excess hydrochloric acid, and the hydrogen liberated was collected over water at 26.5°C . and 760 mm. pressure. The combining weight of Zn is 32.685. Calculate the volume of dry hydrogen liberated at given temperature and pressure. Vapor pressure of water at 26.5°C . = 25.7 mm.
Ans. 787.6 cc.

- 524.** A sample of Al weighing 1.025 g. was treated with excess dilute sulfuric acid. The hydrogen evolved was collected over Hg at 22°C. and 748 mm. pressure. The combining weight of Al is 9.033. Calculate the volume of hydrogen liberated at the given temperature and pressure. *Ans.* 1,390 cc.
- 525.** Calculate the number of grams of each of the following compounds required to make 1 l. of a *N* solution of that compound: (a) $\text{H}_2\text{C}_2\text{O}_4$, (b) CaCl_2 , (c) Li_2SO_4 , (d) BiCl_3 .
Ans. (a) 45.008 g.; (b) 55.5 g.; (c) 54.97 g.; (d) 105.127 g.
- 526.** Calculate the number of grams of each of the following compounds required to make 500 cc. of 2.5 *N* solution of that compound: (a) NH_4OH , (b) HClO_3 , (c) Rb_2SO_4 , (d) $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.
Ans. (a) 43.8 g.; (b) 105.58 g.; (c) 166.85 g.; (d) 203.28 g.
- 527.** Calculate the number of grams of each of the following compounds required to make 1 l. of 0.0125 *N* solution of that compound: (a) KMnO_4 as an oxidizer in acid solution, (b) KOH , (c) H_2SO_4 , (d) Li_3PO_4 .
Ans. (a) 0.395 g.; (b) 0.7013 g.; (c) 0.6129 g.; (d) 0.4827 g.
- 528.** How many grams of H_2SO_4 is contained in (a) 25 cc. of 0.9875 *N* H_2SO_4 , (b) 50 cc. of 0.05 *N* H_2SO_4 ? *Ans.* (a) 1.2106 g.; (b) 0.1225 g.
- 529.** How many grams of HNO_3 is contained in (a) 30.5 cc. of 0.4580 *N* HNO_3 , (b) 45.0 cc. of 0.1 *N* HNO_3 ? *Ans.* (a) 0.8801 g.; (b) 0.2835 g.
- 530.** How many cubic centimeters of sulfuric acid (sp. gr. 1.8354 and containing 93.19 per cent by weight of H_2SO_4) is necessary to make 1 l. of 0.4 *N* H_2SO_4 ? *Ans.* 11.46 cc.
- 531.** Calculate the number of cubic centimeters of sodium carbonate solution (sp. gr. 1.19 and containing 17.9 per cent by weight of Na_2CO_3) required to make 250 cc. of 0.5 *N* Na_2CO_3 . *Ans.* 31.10 cc.
- 532.** Calculate the number of cubic centimeters of hydrochloric acid solution (sp. gr. 1.2 and containing 39.11 per cent by weight of HCl) required to make 1 l. of 6 *N* HCl . *Ans.* 466.1 cc.
- 533.** Calculate the number of cubic centimeters of 0.4 *N* AgNO_3 that can be obtained by dissolving 13.590 g. of silver nitrate in water. *Ans.* 200 cc.
- 534.** Calculate the number of cubic centimeters of 0.05 *N* KMnO_4 solution that can be made by dissolving 0.3950 g. of potassium permanganate in water, when used as an oxidizer. *Ans.* 250 cc.
- 535.** Calculate the number of cubic centimeters of 0.4 *N* $\text{K}_2\text{Cr}_2\text{O}_7$ solution, when used as an oxidizer that can be made by dissolving 3.9226 g. of potassium dichromate in water. *Ans.* 200 cc.
- 536.** Calculate the normality of a solution of potassium hydroxide that contains the equivalent of 0.6850 g. of OH in 44 cc. of the solution. *Ans.* 0.9153 *N*.
- 537.** Calculate (a) the normality of a solution of sulfuric acid that contains 3.56 g. of SO_3 per liter of solution; (b) the normality of a sodium carbonate solution that contains 3.875 g. of Na_2O in 300 cc. of solution. *Ans.* (a) 0.0889 *N*; (b) 0.4136 *N*.

- 538.** Calculate (a) the normality of a solution of barium hydroxide that contains 7 g. of BaO in 500 cc. of solution; (b) the normality of ammonium hydroxide that contains 8.885 g. of NH_3 in 250 cc. of solution.
Ans. (a) 0.1825 *N*; (b) 2.087 *N*.

Additional Problems without Answers, for Quizzes

- 539.** Calculate the combining weights of the metals in each of the following compounds: (a) stannous oxide, (b) stannic oxide, (c) antimony trisulfide, (d) cadmium sulfide, (e) mercuric oxide.
- 540.** Calculate the combining weights of the metals in each of the following compounds: (a) aluminum carbide, (b) calcium phosphide, (c) silver sulfide, (d) lithium nitride, (e) chromic oxide.
- 541.** Calculate the combining weights of the metals in each of the following compounds: (a) Mg_3N_2 , (b) GeO, (c) WO_2 , (d) MoS_2 , (e) Cu_2S .
- 542.** Calculate the combining weights of the metals in each of the following compounds: (a) Cu_2F_2 , (b) Co_2O_3 , (c) CrF_2 , (d) Ca_3N_2 , (e) Be_2C .
- 543.** Calculate the gram-equivalent of each of the following: (a) BaCrO_4 , (b) $\text{Mg}_2\text{P}_2\text{O}_7$, (c) $\text{Ca}(\text{MnO}_4)_2$ as an oxidizer, (d) SnCl_2 as a reducer, (e) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ as an oxidizer.
- 544.** Calculate the gram-equivalent of each of the following: (a) $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, (b) $(\text{NH}_4)_2\text{PtCl}_6$, (c) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, (d) FeCl_2 as a reducer.
- 545.** Calculate the gram-equivalent of each of the following: (a) $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, (b) PbCrO_4 , (c) $\text{Fe}_2(\text{SO}_4)_3$ as an oxidizer, (d) NaIO_3 as an oxidizer, (e) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.
- 546.** Calculate the gram-equivalent of each of the following: CaCl_2 ; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.
- 547.** Calculate the gram-equivalent of each of the following: CuSO_4 ; $\text{CuSO}_4 \cdot \text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
- 548.** When water reacts with 10 g. of sodium, 4,869.5 cc. of hydrogen is generated at 0°C . and 760 mm. pressure. Calculate the combining weight of sodium from this fact.
- 549.** A piece of iron weighing 25 g. was immersed for some time in a solution of CuSO_4 . After removing, it was found to have lost 3.15 g. By the action that took place, 3.586 g. of copper was displaced. The combining weight of Fe is 27.92. Calculate the combining weight of Cu.
- 550.** Calculate the combining weight of a metal 6.775 g. of which yielded 0.756 g. of hydrogen at 0°C . and 760 mm. pressure.
- 551.** The combining weight of a certain metal is 23.0. Calculate the volume of hydrogen, measured over water at 22°C . and 750 mm. pressure, that will be liberated by 3.0 g. of this metal. Vapor pressure of water at 22°C . = 19.7 mm.
- 552.** When 4 g. of a metal M was dissolved in sulfuric acid, 900 cc. of hydrogen was liberated, measured over water at 20°C . and at a barometric pressure of 752 mm. Calculate the combining weight of metal M. Vapor pressure of water at 20°C . = 17.4 mm.

- 553.** The combining weight of a certain metal is 8.99. Calculate the volume of hydrogen measured over water at 21°C. and 753 mm. pressure that will be displaced by 1.25 g. of this metal when treated with an acid. Vapor pressure of water at 21°C. = 18.5 mm.
- 554.** Calculate the combining weight of a metal, 0.3288 g. of which yielded 0.472 l. of hydrogen, collected over water at 22°C. and 750 mm. pressure. Vapor pressure of water at 22°C. = 19.7 mm.
- 555.** Calculate the combining weight of (a) bismuth in bismuth oxide that contains 89.65 per cent of Bi and 10.35 per cent of O; (b) mercury in mercuric oxide that contains 92.61 per cent of Hg and 7.39 per cent of O; (c) manganese in manganous oxide that contains 77.44 per cent of Mn and 22.56 per cent of O.
- 556.** The combining weight of a certain metal M is 32.5. Calculate the volume of hydrogen liberated when collected over water at 28°C. and 748 mm. pressure, by action of an acid on 2.029 g. of the metal. Vapor pressure of water at 28°C. = 28.1 mm.
- 557.** Calculate the combining weight of a metal M that is treated with excess hydrochloric acid, the hydrogen displaced being collected in a flask over water. Use the following data:

Weight of metal taken..... 0.625 g.
 Weight of water displaced by the hydrogen evolved..... 850.0 g.

Level of water inside the flask is 3 in. above the outside level.

Barometric pressure..... 745.0 mm.
 Temperature..... 20.0°C.
 Vapor pressure of water at 20°C..... 17.4 mm.
 Weight of 1 l. of hydrogen at 0°C., 760 mm..... 0.0898 g.

(Neglect the solubility of hydrogen in the water.)

- 558.** Calculate the combining weight of a metal treated with excess hydrochloric acid, the hydrogen displaced being collected in a flask over water. Use the following data:

Weight of metal taken..... 2.541 g.
 Weight of water displaced by the hydrogen evolved..... 963.66 g.

Level of water inside the flask is 2 in. above the outside level.

Barometric pressure..... 758.0 mm.
 Temperature..... 21.0°C.
 Vapor pressure of water at 21°C..... 18.5 mm.
 Weight of 1 l. of hydrogen at 0°C., 760 mm..... 0.0898 g.

(Neglect the solubility of hydrogen in water.)

- 559.** Calculate the combining weight of a metal that is treated with excess hydrochloric acid, the hydrogen displaced being collected in a graduate over water. Use the following data:

Weight of metal taken.....	0.2022 g.
Volume of hydrogen collected.....	78.76 cc.

Level of water inside the flask is 20 mm. above the outside level.

Barometric pressure.....	760.0 mm.
Temperature.....	25.5°C.
Vapor pressure of water at 25.5°C.....	24.27 mm.
Weight of 1 l. of hydrogen at 0°C., 760 mm.....	0.0898 g.

(Neglect the solubility of hydrogen in water.)

- 560.** Calculate the combining weight of a metal treated with excess dilute sulfuric acid, the hydrogen displaced being collected in a flask over water. Use the following data:

Weight of metal taken.....	1.025 g.
Weight of water displaced by the hydrogen evolved....	1,300.0 g.

Level of water inside the flask is 100 mm. above the outside level.

Barometric pressure.....	748.0 mm.
Temperature.....	22.0°C.
Vapor pressure of water at 22°C.....	19.66 mm.
Weight of 1 l. of hydrogen at 0°C., 760 mm.....	0.898 g.

(Neglect the solubility of hydrogen in water.)

- 561.** When phosphorus trichloride comes in contact with water it is completely hydrolyzed forming phosphorous acid and hydrochloric acid. It was found that when 2.35 g. of phosphorus trichloride was decomposed by water, and when AgNO_3 had been added to this solution, the precipitate of AgCl obtained weighed 7.353 g. The combining weight of Ag is 107.88, and that of Cl is 35.46. From these data calculate the combining weight of phosphorus.
- 562.** Calculate the number of grams of each of the following compounds required to make 500 cc. of 0.15 *N* solution of that compound: (a) Na_3AsO_4 , (b) HgCl_2 , (c) LiOH , (d) HBr .
- 563.** Calculate the number of grams of each of the following compounds required to make 250 cc. of 0.4 *N* solution of that compound: (a) Na_2HPO_4 , (b) KI , (c) K_2CO_3 , (d) $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.
- 564.** Calculate the number of grams of each of the following compounds required to make 2.5 l. of 0.1 *N* solution of that compound: (a) $\text{Na}_2\text{Cr}_2\text{O}_7$ as an oxidizer, (b) $\text{Na}_2\text{Cr}_2\text{O}_7$ as a precipitating agent, (c) $\text{Fe}_2(\text{SO}_4)_3$ as an oxidizer, (d) SnCl_2 as a reducing agent, (e) $\text{Ca}(\text{MnO}_4)_2$ as an oxidizer.
- 565.** How many grams of H_2SO_4 is contained in (a) 50 cc. of 36 *N* H_2SO_4 , (b) 25 cc. of 0.4 *N* H_2SO_4 ?
- 566.** How many grams of HNO_3 , when used as an oxidizer, is contained in (a) 50 cc. of 8 *N* HNO_3 , (b) 25 cc. of 4.385 *N* HNO_3 ? Assume the reduction of NO_3^- to NO .

567. Calculate the normality of (a) dilute hydrochloric acid that has a specific gravity of 1.10 and contains 20.0 per cent by weight of HCl, (b) ammonium hydroxide solution that has a specific gravity of 0.8946 and contains 30.38 per cent by weight of NH_3 .
568. Calculate the volume of potassium hydroxide solution (sp. gr. 1.546 and containing 50.6 per cent by weight of KOH) necessary to prepare 500 cc. of 0.1 N KOH solution.
569. What volume of nitric acid (sp. gr. 1.255 and containing 40.58 per cent by weight of HNO_3) is necessary to prepare 10 l. of 0.25 N HNO_3 , when used as an ordinary acid?
570. How many mols of phosphoric acid is contained in 5 l. of 2.7 N H_3PO_4 ?
571. Calculate (a) the normality of concentrated sulfuric acid that has a specific gravity of 1.8437 and contains 98 per cent by weight of H_2SO_4 ; (b) the normality of concentrated nitric acid solution that has a specific gravity of 1.42 and contains 69.8 per cent HNO_3 by weight.
572. Calculate the number of cubic centimeters of phosphoric acid solution (sp. gr. 1.426 and 60 per cent by weight of H_3PO_4) required to prepare 5 l. of 5 N H_3PO_4 .
573. Calculate the normality of syrupy phosphoric acid (sp. gr. 1.689 and containing 85 per cent by weight of H_3PO_4).
574. Determine the number of cubic centimeters of phosphoric acid solution (sp. gr. 1.426 and containing 43.5 per cent by weight of P_2O_5) necessary to make 500 cc. of 3 N H_3PO_4 .
575. Find (a) the normality and (b) the molarity of the following solutions:
- (i) 3 cc. of 6 N HCl diluted to 100 cc.
 - (ii) 3 cc. of HCl (sp. gr. 1.2 and 40 per cent by weight of HCl) diluted to 100 cc.
 - (iii) 49 g. of H_2SO_4 in 250 cc. of solution.
 - (iv) 10 cc. of 3 M H_3PO_4 diluted to 100 cc.
576. The normality of concentrated stock reagents is as follows: HCl is 12 N ; HNO_3 is 16 N ; H_2SO_4 is 36 N ; NH_4OH is 15 N . Determine the number of cubic centimeters of stock reagent necessary to prepare 10 cc. of each of the following solutions: 5 N NH_4OH ; 9 N H_2SO_4 ; 6 N HNO_3 ; 3 N HCl; 1.2 N H_2SO_4 .

CHAPTER X

OUTLINE

Estimation of the weight of HNO_3 in each cubic centimeter of commercial nitric acid.

Examples of titration. Determination of the percentage of NaCl in table salt by titration.

Relations of normal solutions to one another.

The weight of a substance necessary to make a given volume of a standard solution is found by calculations based on atomic weights. The solution is made up on the basis of these calculations. The exact strength of the solution is then determined by experiment. This last step is called *standardization*.

VOLUMETRIC ANALYSIS

In many of the processes carried out in science and industry, it is important to know accurately the strength of reagents employed. Thus, in the preparation of silver nitrate for use in moving-picture films, the strength of the nitric acid is nicely adjusted to the silver.

The nitric acid arrives at the plant in glass vessels (carboys). A small quantity of it is taken to the laboratory for examination. We want to know how much HNO_3 there is in each unit of volume (say, each cubic centimeter) of the commercial nitric acid. It will do no harm and will be found convenient first to dilute the commercial acid; thus, 25 cc. of it may be diluted to 1,000 cc. with pure water, giving a ratio of 40:1. The 25 cc. is measured very accurately and very conveniently by means of a graduated tube called a burette. A common type having a capacity of 50 cc. is shown in Fig. 15.

To determine the weight of HNO_3 in each cubic centimeter of the diluted nitric acid, we measure out some of it very accurately from a burette and then find how much NaOH is required to just neutralize this amount of the diluted nitric acid. For example, if we have a solution of sodium hydroxide that contains 0.0142 g. of NaOH in each cubic centimeter, and we find by

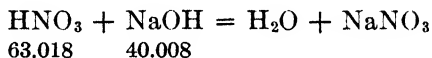
experiment that 28.7 cc. of this NaOH solution is required to just neutralize the HNO_3 in 25.6 cc. of the diluted nitric acid, then, since these are the quantities that exactly neutralized one another, they are chemically equal. That is, 25.6 cc. of diluted nitric acid solution equals 28.7 cc. of the NaOH solution.

$$1.0 \text{ cc. of diluted nitric acid solution} = \frac{28.7}{25.6} =$$

1.121 cc. of NaOH solution

But 1 cc. of the NaOH solution contains 0.0142 g. of NaOH.

One cubic centimeter of the diluted nitric acid solution therefore equals 1.121×0.0142 , or 0.0159 g. of NaOH. Now, the equation



shows that 40.008 g. of NaOH reacts with and neutralizes 63.018 g. of HNO_3 .

One gram of NaOH will therefore neutralize $63.018/40.008$, or 1.575 g. of HNO_3 ; and 0.0159 g. of NaOH therefore neutralizes 0.0159×1.575 , or 0.0250 g. of HNO_3 . That is, 1 cc. of the diluted nitric acid, which by this experiment equals 0.0159 g. of NaOH, must contain 0.025 g. of HNO_3 .

The original commercial nitric acid was diluted in the ratio of 1 cc.:40 cc. to make this diluted acid. The commercial nitric acid, as received at the plant, therefore contains 40×0.0250 , or 1.00 g. of HNO_3 per cubic centimeter.

This process by which the strength of the commercial nitric acid was determined is known as **titration**. The chemist would say he had titrated the nitric acid with NaOH, meaning that he determined the strength of the nitric acid by measuring the volume of NaOH solution of known strength required to neutralize a given volume of it.

In thousands of laboratories all over the world one of the duties of the analytical chemist is to titrate liquids of all kinds. Titration is used to determine the strength of acids like nitric and to determine the amount of acid in vinegar and in a great variety

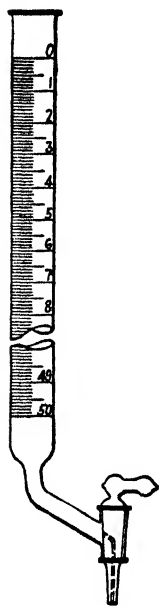
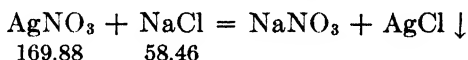


FIG. 15.

of other liquids and juices. Furthermore, it is not limited to finding the amount of acid. We could reverse the process and could determine the amount of alkali, in a soap liquid, for example. To do this we should take a solution of HCl that contained a known weight of HCl in each cubic centimeter and should find how many cubic centimeters of this solution were necessary to neutralize each cubic centimeter of the alkaline liquid.

Furthermore titration is not even limited to acids and bases. Suppose that we wanted to know how much sodium chloride, NaCl, there is in a sample of table salt. We should put in a burette a solution of silver nitrate containing a known amount, say 24.0 g., of silver nitrate in 1,000 cc. of solution. When silver nitrate is added to sodium chloride, a reaction takes place: Sodium nitrate and silver chloride are formed. The silver chloride formed is not soluble in the solution and is therefore precipitated. Experiments have shown that 169.88 parts by weight of silver nitrate is necessary to react with 58.46 parts by weight of sodium chloride to form sodium nitrate and silver chloride. This is repeated by the equation



We should weigh accurately a small portion of the table salt. Say the weight of table salt thus taken was 0.2068 g. We should dissolve this in water and should then add the silver nitrate solution from the burette, a few drops at a time, until just enough had been added to precipitate all the NaCl.

We then observe the level of the solution in the burette. Suppose that 19.0 cc. of silver nitrate solution has been required. Then, since there is 0.0240 g. of silver nitrate in 1 cc. of the silver nitrate solution, $19.0 \times 0.024 = 0.456$ g. of silver nitrate, the amount necessary to react with the sodium chloride.

The experiments on which the foregoing equation is based showed us that 1 gram-mol or 169.88 g. of silver nitrate was necessary to react with 1 gram-mol, or 58.46 g., of NaCl.

1 g. of silver nitrate is necessary for $1/169.88 \times 58.46$ g. NaCl.

0.456 g. of silver nitrate is necessary for $0.456 \times 58.46/169.88$, or 0.1569 g. NaCl.

In 0.2068 g. of the table salt there is 0.1569 g. of NaCl.

In 1 g. of the table salt there is $1/0.2068 \times 0.1569$, or 0.7587 g. of NaCl.

In 100 g. of the table salt there is 100×0.7587 , or 75.87 g. of NaCl.

In general, titration is a very convenient method for the analysis of substances. Solutions are used that contain weighed amounts of the titrating substance in each liter of solution.

RELATION OF NORMAL SOLUTIONS TO ONE ANOTHER

Since the gram-equivalent of any acid contains 1.008 g. of ionizable hydrogen, and since the gram-equivalent of any base contains 17.008 g. of OH, it follows that one gram-equivalent of any acid will completely neutralize one gram-equivalent of any base. Also, 1 l. of a normal solution of any acid must be equivalent to 1 l. of a normal solution of any base, or

1 cc. of a N solution of any acid \approx 1 cc. of a N solution of any base

Since normal solutions of all substances contain one gram-equivalent of the substance dissolved in 1 l. of solution (not of solvent) in each case, this principle can be applied generally to all substances. That is,

1 cc. of a N solution of any substance \approx 1 cc. of a N solution of any other substance

The following problems will illustrate the general application of this principle.

Example 1.—Calculate the number of cubic centimeters of a 0.1 N H_2SO_4 solution necessary to neutralize a solution that contains 0.125 g. of Na_2CO_3 .

Starting with the premise that 1 cc. of any N solution \approx 1 cc. of any other N solution, it follows that

1 cc. 0.1 N $H_2SO_4 \approx$ 1 cc. 0.1 N Na_2CO_3

Since our problem states that the solution contains 0.125 g. of Na_2CO_3 , the first step in solving it is to calculate the number of cubic centimeters of 0.1 N Na_2CO_3 solution that contains 0.125 g. of Na_2CO_3 .

The chemical equivalent of Na_2CO_3 is equal to one-half the molecular weight of Na_2CO_3 , or $106/2 = 53.0$. A N Na_2CO_3

solution would then contain 53.0 g. of Na_2CO_3 per liter (1,000 cc.). A 0.1 *N* solution of Na_2CO_3 (0.1 *N* Na_2CO_3) would contain 5.3 g. of Na_2CO_3 per liter of solution, or 5.3 g./1,000 cc. = 0.0053 g. Na_2CO_3 in 1 cc. 0.1 *N* Na_2CO_3 .

There would be 1 g. Na_2CO_3 in $1/0.0053$ cc. of 0.1 *N* Na_2CO_3 and 0.125 g. Na_2CO_3 in $0.125 \times 1/0.0053 = 23.58$ cc. of 0.1 *N* Na_2CO_3 .

Since 0.125 g. of Na_2CO_3 is contained in 23.58 cc. of 0.1 *N* Na_2CO_3 solution, and 1 cc. of 0.1 *N* $\text{Na}_2\text{CO}_3 \approx 1$ cc. of 0.1 *N* H_2SO_4 , then 23.58 cc. of 0.1 *N* $\text{Na}_2\text{CO}_3 \approx 23.58$ cc. of 0.1 *N* H_2SO_4 ; i.e., it will require 23.58 cc. of 0.1 *N* H_2SO_4 to neutralize a solution containing 0.125 g. of Na_2CO_3 .

An alternate method that is available for the solution of this problem is based on the following relationship:

$$\text{Normality} = \frac{\text{number of gram-equivalents}}{\text{number of liters}} \quad (1)$$

or

$$\text{Normality} = \frac{\text{number of milligram-equivalents}}{\text{number of cubic centimeters}} \quad (2)$$

Then

$$\text{Number of gram-equivalents} = \text{number of liters} \times \text{normality} \quad (3)$$

or

$$\text{Number of milligram-equivalents} = \frac{\text{number of cubic centimeters} \times \text{normality}}{\quad} \quad (4)$$

Step 1.—Determine how many milligram-equivalents of Na_2CO_3 is contained in 0.125 g. of Na_2CO_3 .

The chemical equivalent of $\text{Na}_2\text{CO}_3 = 106\frac{1}{2} = 53.0$

Then

53.0 g. $\text{Na}_2\text{CO}_3 = 1$ gram-equivalent of Na_2CO_3

0.125 g. $\text{Na}_2\text{CO}_3 = 0.125 \times \frac{1}{53.0} = 0.002358$ gram-equivalent of Na_2CO_3

0.002358 gram-equivalent = 2.358 milligram-equivalents of Na_2CO_3 .

Step 2.

1 gram-equivalent of $\text{Na}_2\text{CO}_3 = 1$ gram-equivalent of H_2SO_4

or

1 milligram-equivalent of Na_2CO_3 = 1 milligram-equivalent of H_2SO_4

Therefore,

2.358 milligram-equivalents of Na_2CO_3 = 2.358 milligram-equivalents of H_2SO_4

Step 3.—Applying formula (4), and letting x = the number of cubic centimeters of 0.1 N H_2SO_4 ,

$$2.358 = x \text{ cc.} \times 0.1$$

$$x = 23.58 \text{ cc. of } 0.1 \text{ } N \text{ } \text{H}_2\text{SO}_4$$

In many of the following problems the weight of substance required to make a given volume of, say, a normal solution is to be calculated. It must be noted, however, that many chemicals rated as chemically pure (C.P.) do not contain 100 per cent of the substance indicated on the label. Furthermore, it would be highly inaccurate to make up a N solution of an acid such as HCl by calculations based on the specific gravity of the acid and the HCl content corresponding to this as derived from specific gravity tables.

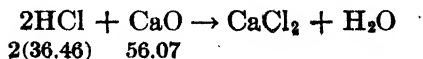
For this reason, the solution is made up on the basis of calculations as indicated, and then its exact strength is almost invariably determined by experiment. For example, a solution of hydrochloric acid would be made up approximately normal on the basis of calculations, and then the exact strength of this solution might be determined by finding how many cubic centimeters of it were required to react with a definite weight of very pure Na_2CO_3 . The procedure of determining the exact strength of a solution is spoken of as **standardization**.

Example 2.—Calculate (a) the weight of HCl ; (b) the number of cubic centimeters of hydrochloric acid (sp. gr. 1.2 and containing 39.11 per cent by weight of HCl) that will be necessary to make 2 l. of a hydrochloric acid solution of such strength that 1 cc. of this acid is equivalent to 0.001 g. CaO .

In the solution of this problem, part (a) will be solved by three different methods.

(a) *Method I.*—The hydrochloric acid solution is to be evaluated so that 1.0 cc. of the acid \approx 0.001 g. CaO .

From the reaction



we obtain the relation that 1 gram-mol, or 56.07 g., of CaO requires 2 gram-mols, or 2(36.46) g. of HCl for complete neutralization. Then

1.0 g. of CaO requires $1/56.07 \times 2(36.46)$ g. HCl.

0.001 g. of CaO requires $0.001 \times \frac{1}{56.07} \times 2(36.46)$ g. =
0.0013 g. HCl.

That is, there must be 0.0013 g. HCl in 1 cc. of our hydrochloric acid solution, but we wish to make 2 l. of this solution, so that $2,000 \times 0.0013 = 2.60$ g. of HCl will be required.

(a) *Method II.*—Solving the problem on the basis of equivalent relations.

First determine the number of gram-equivalents contained in 0.001 g. of CaO.

The equivalent weight of CaO is one-half the molecular weight of CaO, or $56.07/2 = 28.035$; *i.e.*, 28.035 g. of CaO is contained in 1 gram-equivalent of CaO.

1 g. of CaO is contained in $1/28.035$ gram-equivalent of CaO.

0.001 g. of CaO is contained in $0.001 \times 1/28.035 = 0.0000357$ gram-equivalent of CaO. Since 1 gram-equivalent weight of CaO is equivalent to 1 gram-equivalent weight of HCl, then 0.0000357 gram-equivalent of CaO = 0.0000357 gram-equivalent of HCl.

1 gram-equivalent of HCl = 36.46 g. of HCl
and

0.0000357 gram-equivalent of HCl = $0.0000357 \times 36.46 =$
0.0013 g. of HCl

This is the weight of HCl that must be contained in 1 cc. of solution, so that 1 cc. of the acid is equivalent to 0.001 g. of CaO. However, as 2 l. is asked for in the problem, $2,000 \times 0.0013$ g. = 2.60 g. of HCl will be needed. Note this is in agreement with the answer for this part of the problem using Method I.

(a) *Method III.*—Solving the problem by normality relations.

1.0 cc. of N CaO \approx 1.0 cc. of N HCl

The equivalent weight of CaO is one-half its molecular weight, or $56.07/2 = 28.035$. Then, theoretically, N CaO = 28.035 g. per liter. N CaO = 0.028035 g. CaO per cubic centimeter.

To determine the normality of a solution that contains 0.001 g. of CaO per cubic centimeter, it is necessary only to compare this amount (0.001 g.) with the amount contained in 1.0 cc. of a N CaO solution, or 0.028035 g. CaO. Our solution is

$$\frac{0.001}{0.028035} = 0.0357 \text{ times as strong as a } N \text{ solution}$$

0.001 g. CaO per cubic centimeter corresponds, therefore, to 0.0357 N CaO. But 1.0 cc. of 0.0357 N CaO \approx 1.0 cc. of 0.0357 N HCl.

We are asked to make up 2 l. of a solution = 0.001 g. CaO per cubic centimeter = 0.0357 N HCl. It is then necessary to calculate the number of grams of HCl required to make 2 l. of 0.0357 N HCl.

Since N HCl contains 36.46 g. of HCl per liter,

1 l. of 0.0357 N HCl will contain 0.0357×36.46 g. of HCl.

2 l. of 0.0357 N HCl will contain $2 \times 0.0357 \times 36.46 = 2.60$ g. of HCl.

Note that this number agrees with the number obtained by each of the other methods of solution.

(b) The commercial hydrochloric acid has a specific gravity of 1.2 and contains 39.11 per cent by weight of HCl. Then there will be $1.2 \times 0.3911 = 0.4693$ g. of actual HCl in 1.0 cc. of this hydrochloric acid solution.

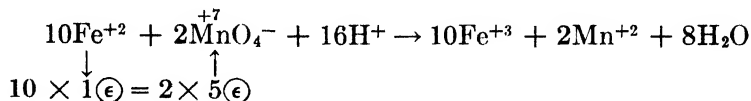
Since there is 0.4693 g. of HCl in 1.0 cc. of hydrochloric acid solution, there will be 1 g. of HCl in $1/0.4693 \times 1.0$ cc. of hydrochloric acid solution, and 2.6 g. of HCl in $2.6 \times 1/0.4693 = 5.54$ cc. of commercial hydrochloric acid.

That is to say, 5.54 cc. of hydrochloric acid (sp. gr. 1.2 and containing 39.11 per cent by weight of HCl) must be diluted with sufficient distilled water to make 2 l., in order that each 1 cc. of the acid may be equivalent to 0.001 g. of CaO.

OXIDATION AND REDUCTION

Example 3.—A solution of ferrous sulfate acidified with sulfuric acid is to be titrated with KMnO_4 solution. Calculate the number of grams of KMnO_4 needed per liter of solution so that 1 cc. of KMnO_4 solution will be equivalent to 0.005 g. of Fe.

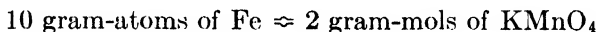
Solution.—The foregoing reaction is one involving oxidation and reduction. The ferrous ion, Fe^{+2} , is oxidized to the ferric condition Fe^{+3} by the permanganate ion, MnO_4^- , which, in turn, is reduced to the manganous ion, Mn^{+2} . This can be represented by



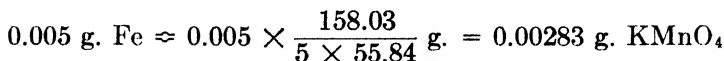
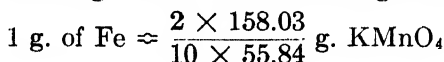
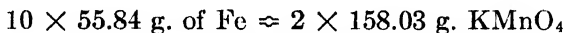
We are interested chiefly in the amount of Fe in the ferrous sulfate. From the foregoing equation we can state that



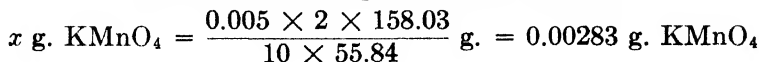
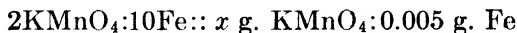
or



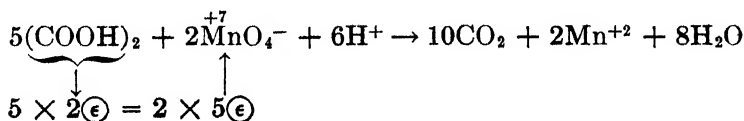
Then



Alternate method of setting up the foregoing relations, sometimes used in calculations in quantitative analytical methods: From the preceding equation it is readily seen that 2 gram-mols of KMnO_4 can react with 10 gram-atoms of Fe, or $2\text{KMnO}_4 \approx 10\text{Fe}$. The following proportion can be set up:



Example 4.—How many grams of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ or $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, will be required to react with 50.0 cc. of 1.055 *N* KMnO_4 solution acidified with sulfuric acid?



Method A. Step 1.—Determine the number of grams of KMnO_4 contained in 50.0 cc. of 1.055 *N* KMnO_4 .

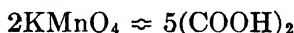
It is to be observed in the foregoing skeleton equation that the gram-equivalent of KMnO_4 is one-fifth its gram-molecular weight, or $158.03/5 \text{ g.} = 31.606 \text{ g.}$ Then *N* KMnO_4 (as an oxidizer) contains 31.606 g. KMnO_4 per liter.

1.055 *N* KMnO_4 will contain $1.055 \times 31.606 \text{ g.}$ KMnO_4 per liter, or

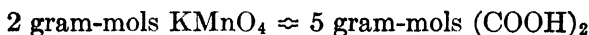
$$\frac{50}{1,000} \times 1.055 \times 31.606 \text{ g. } \text{KMnO}_4 \text{ per 50.0 cc. of solution}$$

$$= 1.667 \text{ g. } \text{KMnO}_4 \text{ in 50.0 cc. of 1.005 } N \text{ } \text{KMnO}_4.$$

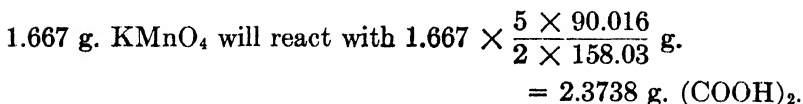
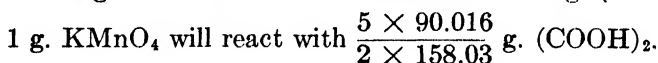
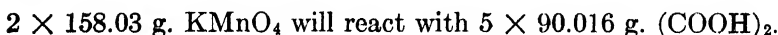
Step 2.—From the preceding skeleton equation it is also seen that



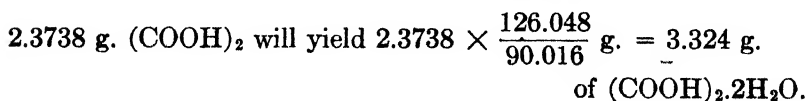
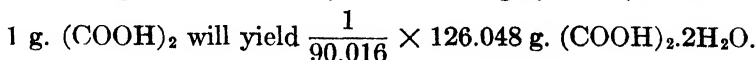
or



Then



Step 3.—Since 1 gram-mol of $(\text{COOH})_2$ will yield 1 gram-mol $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, or



Method B.—A much simpler method based on the principle of the equivalency of normal solutions can be employed in the solution of this problem. Thus, 1 cc. of any normal solution \approx 1 cc. of any other normal solution, or 50.0 cc. of 1.055 *N* $\text{KMnO}_4 \approx$

50.0 cc. of 1.055 N $H_2C_2O_4 \cdot 2H_2O$. It is necessary then only to calculate the weight of $H_2C_2O_4 \cdot 2H_2O$ present in 50.0 cc. of 1.055 N $H_2C_2O_4 \cdot 2H_2O$.

We note from the equation above that oxalic acid, $H_2C_2O_4$, is a reducing agent. The gram-equivalent of this compound ($H_2C_2O_4 \cdot 2H_2O$) as obtained from the equation would be one-half its gram-molecular weight, or $126.048/2$ g. = 63.024 g.

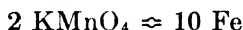
The gram-equivalent of $H_2C_2O_4 \cdot 2H_2O$ = 63.024 g. Then

N $H_2C_2O_4 \cdot 2H_2O$ contains 63.024 g. of $H_2C_2O_4 \cdot 2H_2O$ per liter of solution, and

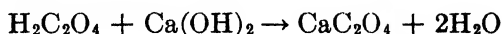
1.055 N $H_2C_2O_4 \cdot 2H_2O$ contains 1.055×63.024 g. of $H_2C_2O_4 \cdot 2H_2O$ per liter.

50.0 cc. of 1.055 N $H_2C_2O_4 \cdot 2H_2O$ then contains $50/1,000 \times 1.055 \times 63.024$ g. = 3.324 g. of $H_2C_2O_4 \cdot 2H_2O$.

The various separate relationships shown in these examples can be built up as a chain on the basis that things equal to the same thing are equal to each other. Thus,



We also know from the equation



that



We can then write a chain:



This can be extended and used as a convenient means of transition from one type of substance to the equivalent quantity of another.

Problems

577. Calculate the number of cubic centimeters of 2.5 N NaOH solution necessary to neutralize 10 cc. of sulfuric acid, which has a specific gravity of 1.8437 and contains 98.0 per cent by weight of H_2SO_4 .

Ans. 147.3 cc.

578. Calculate the number of cubic centimeters of 0.2 N NH_4OH solution that will exactly neutralize 5 cc. of acetic acid, which has a specific

- gravity of 1.0412 and contains 30 per cent by weight of $\text{HC}_2\text{H}_3\text{O}_2$.
Ans. 130 cc.
579. What weight of BaCl_2 is needed to precipitate completely BaSO_4 from 30.5 cc. of 0.1 H_2SO_4 ?
Ans. 0.3176 g.
580. Calculate the weight of CdS precipitated when 100 cc. of 0.1 N $\text{Cd}(\text{NO}_3)_2$ solution is made ammoniacal and saturated with H_2S .
Ans. 0.7223 g.
581. A solution contains 2.5 g. of $(\text{NH}_4)_2\text{SO}_4$. How many cubic centimeters of 0.4 N BaCl_2 solution would be required to precipitate completely the BaSO_4 in the original solution?
Ans. 94.6 cc.
582. Calculate the normality of a sodium hydroxide solution 35 cc. of which neutralized 34.8 cc. of 0.1234 N HCl .
Ans. 0.1227 N .
583. What is the normality of a potassium hydroxide solution 30 cc. of which neutralized 31.8 cc. of 0.1198 N H_2SO_4 ?
Ans. 0.127 N .
584. A sample of calcite (pure CaCO_3) weighing 1.00 g. required 39.5 cc. of a hydrochloric acid solution for complete neutralization. Calculate the normality of the acid.
Ans. 0.506 N .
585. Calculate the weight of lead sulfate obtained by the action of excess sulfuric acid with 47 cc. of 0.5 N $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.
Ans. 3.563 g.
586. Excess hydrochloric acid precipitated 0.988 g. of AgCl from a given number of cubic centimeters of 0.5 N AgNO_3 solution. Calculate the number of cubic centimeters of 0.5 N AgNO_3 solution that must have been present.
Ans. 13.76 cc.
587. Calculate the number of grams of $\text{K}_2\text{Cr}_2\text{O}_7$ necessary for complete precipitation of PbCrO_4 from 25.0 cc. of 0.2 N $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution. (Hint: 1 gram-mol $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \approx \frac{1}{2}$ gram-mol $\text{K}_2\text{Cr}_2\text{O}_7$).
Ans. 0.3677 g.
588. A solution contains 0.3922 g. of potassium dichromate per 100 cc. Calculate the number of cubic centimeters of 0.4 N $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution that is necessary for complete precipitation of all Cr as lead chromate from 1 l. of this solution.
Ans. 66.6 cc.
589. Calculate the number of cubic centimeters of 0.5 N $\text{K}_4\text{Fe}(\text{CN})_6$ that will be required for complete precipitation of ferric ferrocyanide from a solution containing 1.5 g. of ferric chloride.
Ans. 55.5 cc.
590. Calculate the number of cubic centimeters of 0.1222 N AgNO_3 required to precipitate the chloride from a sample of rock salt weighing 0.2340 g. and containing 99.23 per cent of NaCl .
Ans. 32.5 cc.
591. Convert 32.8 cc. of 0.1452 N H_2SO_4 to the equivalent volume of N H_2SO_4 .
Ans. 4.76 cc.
592. Convert 29.8 cc. of 0.1383 N KOH to the equivalent volume of N KOH .
Ans. 4.12 cc.
593. How many cubic centimeters of 0.1 N KMnO_4 solution would be required to oxidize a solution that contains 0.453 g. of $\text{H}_2\text{C}_2\text{O}_4$?
Ans. 100.6 cc.
594. How many cubic centimeters of 0.2 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution would be required to liberate the chlorine from a solution made acid with concentrated sulfuric acid and containing 1.0 g. of NaCl ?
Ans. 85.5 cc.

595. Calculate the number of grams of FeSO_4 that will be oxidized in a solution acidified with sulfuric acid by 25.8 cc. of 0.1235 N KMnO_4 .
Ans. 0.484 g.
596. Calculate the weight of iodine that will be liberated by the action of 30.5 cc. of 0.2586 N $\text{K}_2\text{Cr}_2\text{O}_7$ with a solution acidified with sulfuric acid and containing an excess of potassium iodide. *Ans.* 1 g.
597. What volume of hydrogen sulfide, at S.T.P., will be required to reduce completely 25.5 cc. of 0.1535 N KMnO_4 , which has been acidified with dilute hydrochloric acid? *Ans.* 87.7 cc.
598. Calculate the number of cubic centimeters of 8 N HNO_3 that would be necessary to dissolve 10 g. of copper turnings. Assume the reduction of NO_3^- to NO . *Ans.* 52.5 cc.
599. Calculate the number of cubic centimeters of 8 N HNO_3 that would be necessary to react completely with 10 g. of Ag_2S . Assume the reduction of NO_3^- to NO , and oxidation of S^{-2} to S^0 . *Ans.* 13.45 cc.
600. (a) Calculate the number of cubic centimeters of 8 N HNO_3 that would be necessary to react completely with 10 g. of As. (b) Calculate the weight of arsenic acid formed in this reaction. Assume the reduction of NO_3^- to NO . *Ans.* (a) 27.83 cc.; (b) 18.93 g.
601. (a) Calculate the number of cubic centimeters of 12 N HCl necessary to react completely with 100 g. of potassium permanganate. (b) Calculate the volume of chlorine collected at 25°C. and 750 mm. pressure by this action. *Ans.* (a) 421.6 cc.; (b) 39.25 l.
602. (a) Calculate the number of cubic centimeters of hydriodic acid (sp. gr. 1.343 and containing 36 per cent by weight of HI) that will react completely with 100 cc. of 0.125 N $\text{K}_2\text{Cr}_2\text{O}_7$. (b) Calculate the weight of iodine obtained by this reaction. *Ans.* (a) 7.68 cc.; (b) 1.585 g.
603. How many cubic centimeters of 0.4 N KOH solution will be necessary to neutralize 10 cc. of the following acids: (a) 0.1 N HCl , (b) 0.1 N H_2SO_4 , (c) 0.05 N H_3PO_4 , (d) N HNO_3 ?
Ans. (a) 2.5 cc.; (b) 2.5 cc.; (c) 1.25 cc.; (d) 25 cc.
604. Excess NH_4OH was added to 100 cc. of a ferric chloride solution. This caused the precipitation of 1.4248 g. of $\text{Fe}(\text{OH})_3$. Calculate the normality of the ferric chloride solution. *Ans.* 0.4 N .
605. Calculate the normality of a nitric acid solution 50.0 cc. of which was neutralized by 48.5 cc. of 0.4 N KOH . *Ans.* 0.388 N .
606. Calculate the number of cubic centimeters of 0.1525 N NaOH required to neutralize 25.5 cc. of 0.1456 N HCl . *Ans.* 24.34 cc.
607. (a) What volume of hydrogen sulfide gas, at S.T.P., is required to precipitate completely the lead from 100 cc. of 0.2 N $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$? (b) What weight of PbS is produced? *Ans.* (a) 224 cc.; (b) 2.3926 g.
608. A solution of ferrous sulfate acidified with sulfuric acid is titrated with $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Calculate the strength of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution if 1 cc. of $\text{K}_2\text{Cr}_2\text{O}_7$ is equivalent to 0.01 g. of Fe . *Ans.* 0.179 N .
609. A solution of ferrous sulfate acidified with sulfuric acid is titrated with KMnO_4 solution. What is the strength of the KMnO_4 solution if 1 cc. of KMnO_4 is equivalent to 0.005 g. of Fe_2O_3 ? *Ans.* 0.0626 N .

610. Calculate the number of cubic centimeters of 0.4980 *N* KOH that is necessary to neutralize 25.0 cc. of 0.2590 *N* H₂SO₄. *Ans.* 13 cc.
611. A solution of nitric acid is 0.2532 *N*. Calculate the number of cubic centimeters of 0.2225 *N* NaOH required to neutralize 15.5 cc. of the acid. *Ans.* 17.65 cc.

Additional Problems without Answers, for Quizzes

612. Calculate the number of cubic centimeters of 0.5 *N* H₂SO₄ that will interact completely with 20 cc. of sodium carbonate solution that has a specific gravity of 1.152 and contains 14.24 per cent by weight of Na₂CO₃.
613. Calculate the number of grams of NaCl necessary for complete precipitation of AgCl from 20.5 cc. of 0.2 *N* AgNO₃ solution.
614. Calculate the weight of AgCl precipitated when 20.0 cc. of 2.5 *N* HCl solution is added to excess AgC₂H₃O₂ solution.
615. How many cubic centimeters of 0.2 *N* HCl will be required to precipitate completely the AgCl from 25.0 cc. of 0.25 *N* AgNO₃ solution?
616. (a) What volume of hydrogen sulfide gas, at S.T.P., is required to precipitate completely the HgS from 75 cc. of 0.1 *N* HgCl₂ solution? (b) What weight of HgS is produced?
617. Excess carbon dioxide is bubbled through 100 cc. of 0.1 *N* Ba(OH)₂ solution. Calculate the weight of BaCO₃ that is precipitated.
618. Excess (NH₄)₂CO₃ was added to 50.0 cc. of a barium acetate solution, forming a precipitate of BaCO₃ which was found to weigh 1.234 g. Calculate the normality of the barium acetate solution.
619. Excess K₂S was added to 75.0 cc. of a hydrochloric acid solution, thereby generating 2,100.0 cc. of hydrogen sulfide, at S.T.P. Calculate the normality of the hydrochloric acid solution.
620. Calculate the normality of a sodium hydroxide solution 35 cc. of which neutralized 46.5 cc. of 0.1 *N* HCl solution.
621. Calculate the number of cubic centimeters of 0.4320 *N* KOH solution necessary to neutralize 20.0 cc. of 0.3870 *N* HNO₃ solution.
622. It was found that in order to neutralize 25.0 cc. of a dilute nitric acid solution, 30.5 cc. of 0.1254 *N* NaOH solution was required. Calculate the normality of the nitric acid solution.
623. It was found that 2.05 cc. of a dilute oxalic acid solution required 22.6 cc. of 0.255 *N* KOH solution for complete neutralization. Calculate the normality of the oxalic acid solution.
624. How many cubic centimeters of 2 *N* H₂SO₄ solution will be required to liberate 500 cc. of SO₂, at S.T.P., by its action with copper turnings?
625. By analysis, a solution of KOH was found to be 0.252 *N*. Calculate how many cubic centimeters of this solution should be taken and diluted with water in order to make 1 l. of 0.1 *N* KOH solution.
626. How many cubic centimeters of a 0.456 *N* HCl solution should be taken and diluted with water in order to prepare 500 cc. of 0.2 *N* HCl? .

627. Give calculations showing how to dilute 1 l. of 0.1 *N* NaOH solution so that each cubic centimeter of the diluted solution will be equivalent to 0.000729 g. of HCl.
628. Calculate the number of cubic centimeters of water necessary to add to 250 cc. of a 1.25 *N* solution in order to make it 0.5 *N*.
629. A sulfuric acid solution contains 0.2198 gram-equivalent of H_2SO_4 per liter. Calculate the number of cubic centimeters of *N* NaOH necessary for the complete neutralization of 20.0 cc. of the acid.
630. A nitric acid solution contains 0.1878 gram-equivalent of HNO_3 per 500 cc. Calculate the number of cubic centimeters of 0.2 *N* KOH necessary for complete neutralization of 10 cc. of the acid.
631. A potassium hydroxide solution contains 0.1237 gram-equivalent of KOH per 500 cc. Calculate the number of cubic centimeters of 0.5 *N* H_2SO_4 that will be required for complete neutralization of 25 cc. of the base.
632. A sodium hydroxide solution contains 0.2456 gram-equivalent of NaOH per liter. Calculate the number of cubic centimeters of 6 *N* $\text{HC}_2\text{H}_3\text{O}_2$ that will be required for complete neutralization of 10 cc. of the base.
633. A barium chloride solution contains 0.1782 gram-equivalent of BaCl_2 per liter. Calculate the number of cubic centimeters of 0.5 *N* $(\text{NH}_4)_2\text{SO}_4$ that will be required for complete precipitation of the Ba^{+2} ion in 10 cc. of the barium chloride solution.
634. In standardizing a hydrochloric acid solution, it was found that 25.8 cc. was required for complete neutralization of a solution containing 1.2588 g. of Na_2CO_3 . Calculate (a) the concentration of HCl in this solution; (b) the normality of this hydrochloric acid solution.
635. In standardizing a sodium hydroxide solution with pure benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$ (equivalent weight, 122.048) it was found that 28.9 cc. of alkali was required for complete neutralization of a solution containing 1.0043 g. of benzoic acid. Calculate the normality of the sodium hydroxide solution.
636. In standardizing a sulfuric acid solution with pure sodium carbonate, it was found that 27.3 cc. of sulfuric acid was required for complete neutralization of 0.1312 g. of Na_2CO_3 . Calculate the normality of the sulfuric acid solution.
637. Calculate the strength of a standard solution of silver nitrate, in order that 1 cc. of this solution may be equivalent to 0.005 g. of chlorine.
638. Calculate the strength of a potassium permanganate solution, in order that 1 cc. of this solution may be equivalent to 0.005 g. of iron.
639. Calculate the number of cubic centimeters of sulfuric acid (sp. gr. 1.5591 and containing 65.13 per cent by weight of H_2SO_4) that will be necessary to make 5 l. of a sulfuric acid solution, so that 1 cc. of this solution is equivalent to 0.005 g. of Na_2O .
640. Calculate the number of cubic centimeters of nitric acid (sp. gr. 1.4216 and containing 70.33 per cent by weight of HNO_3) that will be neces-

sary to make 10 l. of a nitric acid solution, so that 1 cc. of this solution is equivalent to 0.005 g. of NH_3 .

641. A silver nitrate solution is made up so that 1 cc. is equivalent to 0.005 g. of chlorine. Calculate the weight of pure NaCl that must be weighed and dissolved in water so that it requires 30 cc. of the foregoing silver nitrate solution for standardization.
642. A potassium permanganate solution is made up so that 1 cc. is equivalent to 0.005 g. of CaO . Calculate the weight of pure sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, that must be weighed and dissolved in water and then acidified with sulfuric acid, so that it requires 30.5 cc. of the potassium permanganate solution for standardization.
643. A sulfuric acid solution is made up so that 1 cc. is equivalent to 0.005 g. of Na_2O . Calculate the weight of pure sodium carbonate that must be weighed and dissolved in water, so that 40.0 cc. of the sulfuric acid solution is required for complete neutralization.
644. What volume of 0.2530 N H_2SO_4 solution will neutralize 30.0 cc. of 0.1367 N NaOH solution?
645. Calculate the volume of ammonia required to react with 10.0 cc. of 0.1132 N H_2SO_4 solution.
646. How many cubic centimeters of 0.2 N H_2SO_4 is required to neutralize 25.0 cc. of a solution known to contain 25.0 cc. of KOH solution (sp. gr. 1.3440 and 35 per cent by weight of KOH) per liter?
647. Calculate the number of cubic centimeters of 0.1077 N NaOH solution required to neutralize 25.0 cc. of a solution known to contain 20.0 cc. of sulfuric acid (sp. gr. 1.8354 and containing 93.19 per cent by weight of H_2SO_4) per liter.

CHAPTER XI

OUTLINE

The volumes of gases that unite are in simple proportion.

The relative volumes of gases that unite can be seen by inspection of the chemical equation.

Problem. To calculate the volume of oxygen or of air necessary for the combustion of a given volume of a combustible gas.

Gas analysis. Absorption method. Slow-combustion method. The quantitative composition of a mixture of gases can be calculated from a few simple measurements together with inspection of the chemical equation representing the combustion of the gas mixture.

Solution of a gas-analysis problem.

COMBINATION OF GASES

We have seen that an enormous number of experiments on the combination of gases led us to a general law, Gay-Lussac's Law of Volumes. When gases unite, the volumes that unite are in the proportion of simple whole numbers, 1:1; 1:2; 1:3; 1:4; 2:3; etc.; and if the product is a gas, its volume will be in simple proportion with the volumes of the gases that combined.

In Chap. V it was shown that

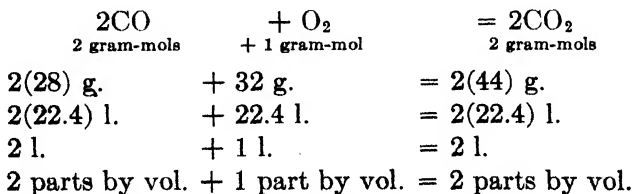
1 gram-mol of any gas occupies 22.4 l. at S.T.P. (molar volume).

1 kilogram-mol of any gas occupies 22.4 cu. m. at S.T.P.

1 ounce-mol of any gas occupies 22.4 cu. ft. at S.T.P.

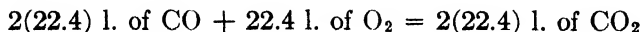
1 pound-mol of any gas occupies 358.4 cu. ft. at S.T.P.

These relations permit us to determine volumes of gases from their molecular weights. Thus, consider the burning of carbon monoxide:



28 g. of CO occupies approximately 22.4 l. at 0°C. and 760 mm.
 32 g. of O₂ occupies approximately 22.4 l. at 0°C. and 760 mm.
 44 g. of CO₂ occupies approximately 22.4 l. at 0°C. and 760 mm.

The actual volumes that combine, when the weights represented by the equation are in grams, are:



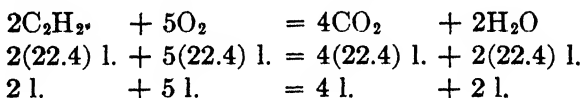
The **relative** volumes represented are

2 parts by vol. of CO + 1 part by vol. of O₂ = 2 parts by vol. CO₂

The parts by volume can be cubic centimeters, liters, gallons, cubic feet, or any other unit of volume. We notice that the volumes that unite are in the same proportion as the number of molecules. This we of course expect, knowing that equal volumes of gases contain equal numbers of molecules at the same condition of temperature and pressure (Avogadro's Law). Each molecule represents 1 part by volume.

Example.—Calculate (a) the volume of oxygen, (b) the volume of air necessary for the complete combustion of 25 l. of acetylene, C₂H₂.

The action is represented by the equation



i.e., the equation indicates that each

2 l. of C₂H₂ unites with 5 l. of O₂ and forms 4 l. of CO₂ and 2 l. of water vapor.

2 l. of C₂H₂ requires for combustion 5 l. of O₂.

1 l. of C₂H₂ requires for combustion $\frac{1}{2} \times 5 \text{ l. of O}_2$.

(a) 25 l. of C₂H₂ requires for combustion $25 \times \frac{5}{2} = 62.5 \text{ l. of O}_2$.

Neglecting the gases present only in small amounts—argon, CO₂, moisture, etc.—air contains

Oxygen.....	20.8 per cent by volume
Nitrogen.....	79.2 per cent by volume

That is, in 100 l. of air there is $\left\{ \begin{array}{l} 20.8 \text{ l. of O}_2 \\ 79.2 \text{ l. of N}_2 \end{array} \right.$

(b) To burn the 25 l. of C_2H_2 required 62.5 l. of oxygen. How much air would be necessary?

There is 20.8 l. of O_2 in 100 l. of air.

There is 1 l. of O_2 in $100/20.8$ l. of air.

There is 62.5 l. of O_2 in $62.5 \times 100/20.8 = 313.4$ l. of air.

We find, then, that from the chemical equation we can calculate the volume of oxygen necessary to unite with a given volume of any combustible gas, and we can also calculate the volume of each of the products formed. Conversely, if we know the volume of the products formed by the combustion of a gas, we can, of course, calculate the volume of the particular gaseous substance that was burned. The equation indicates the **relative** volumes of gases that react and of gaseous products formed. This is of use in gas analysis. We can calculate the volume of each gas in a mixture of gases from a few simple measurements of the volume of the products formed.

GAS ANALYSIS

In this section on Gas Analysis two general methods will be considered. They are generally called (1) the *Absorption Method*; (2) the *Slow-combustion Method*.

Absorption Methods of Gas Analysis.—The absorption method is employed to determine the proportional amounts of the components in a mixture of gases. The general practice is to treat the mixture of gases with different absorbing reagents or absorbents, maintaining a constant temperature and pressure during the entire analysis. The difference in volume of the gas before and after treatment with an absorbent gives the actual volume of the gas absorbed. If the original volume of the sample of gas is 100.0 cc., obviously the amounts absorbed would be directly expressible on a percentage-by-volume basis. If the

ABSORBING REAGENTS	GASES ABSORBED
Strong caustic potash, KOH.....	} Carbon dioxide Sulfur dioxide
Fuming sulfuric acid.....	
	Illuminants (unsaturated hydrocarbons)
Yellow phosphorus	} Oxygen
Alkaline pyrogallol solution }	
Ammoniacal cuprous chloride.....	Carbon monoxide
Palladous chloride solution.....	Hydrogen

original volume is less than 100.0 cc., it is a simple mathematical process to convert each amount into terms of percentage by volume.

The table giving the absorbing reagents and the gases that each reagent will absorb is shown on page 181.

Example.—A sample of a gaseous mixture analyzed by absorption methods for CO_2 , illuminants, O_2 , CO , and N_2 , each measurement made under the same conditions of temperature and pressure, gave the following data:

	CUBIC CENTIMETERS
Volume of sample taken.....	70.5
Volume after treatment with caustic potash.....	66.5
Volume after treatment with fuming sulfuric acid.....	61.5
Volume after treatment with alkaline pyrogallol.....	61.0
Volume after treatment with ammoniacal cuprous chloride.....	51.8

Calculate the percentage of each component in the gaseous mixture.

$$70.5 \text{ cc.} - 66.5 = 4.0 \text{ cc. of } \text{CO}_2$$

$$66.5 \text{ cc.} - 61.5 = 5.0 \text{ cc. of illuminants}$$

$$61.5 \text{ cc.} - 61.0 = 0.5 \text{ cc. of } \text{O}_2$$

$$61.0 \text{ cc.} - 51.8 = 9.2 \text{ cc. of } \text{CO}$$

$$\text{Residual volume} = 51.8 \text{ cc. of } \text{N}_2$$

To express each of these volumes on a percentage basis:

70.5 cc. of gaseous mixture contains 4.0 cc. of CO_2 .

1.0 cc. of gaseous mixture contains $\frac{1}{70.5} \times 4.0$ cc. of CO_2 .

100.0 cc. of gaseous mixture contains $100 \times \frac{1}{70.5} \times 4.0$ cc. =
5.67 cc. of CO_2 .

5.67 cc. in 100 cc. = 5.67 per cent of CO_2

Similarly,

$$100.0 \times \frac{5.0}{70.5} = 7.09 \text{ cc.} = 7.09 \text{ per cent of illuminants}$$

$$100.0 \times \frac{0.5}{70.5} = 0.70 \text{ cc.} = 0.70 \text{ per cent of } \text{O}_2$$

$$100.0 \times \frac{9.2}{70.5} = 13.04 \text{ cc.} = 13.04 \text{ per cent of CO}$$

$$100.0 \times \frac{51.8}{70.5} = 73.47 \text{ cc.} = 73.47 \text{ per cent of N}_2$$

The Slow-combustion Method of Gas Analysis.—The slow-combustion method is employed in gas analysis when a gas mixture contains components that are combustible and particularly when it contains several hydrocarbons. The analytical

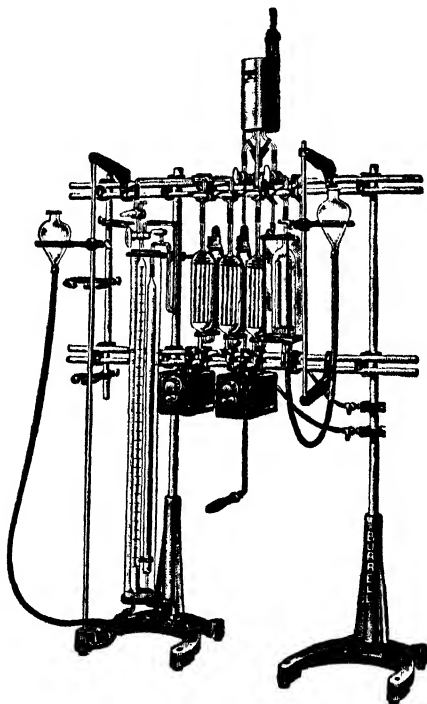


FIG. 16.—Gas-analysis apparatus. (*Burrell.*)

procedure is to introduce a known and sufficient volume of oxygen into what is called a “slow-combustion pipette” (see Fig. 16) and, then, by an electrically heated filament inside the pipette, cause a slow burning of the combustible gas by slowly and gradually transferring a known volume of the gas to the pipette while keeping the wire hot. After the reaction has gone to

completion, the products of combustion are allowed to cool, and their volume is measured. The contraction in volume, as a result of the slow combustion, is noted. The volume of CO_2 obtained from the reaction, and the volume of excess oxygen, are measured by the absorption method. The percentage by volume of each gas is then determined by calculations that will be illustrated by an example later on in this chapter.

When a sample of illuminating gas is to be analyzed, both absorption and slow-combustion methods are employed. It is the usual practice first to pass the gas through each of the various absorption pipettes to remove, respectively, CO_2 , illuminants (unsaturated compounds), and O_2 . After each successive treatment, the contraction in volume is measured and noted. The newer type of gas-analysis apparatus (Fig. 16) also employs copper oxide in a U tube, which might be called an "oxidation tube," for the purpose of oxidizing CO and H_2 simultaneously. After the preliminary absorption measurements, the residual gas is passed over heated copper oxide in the U tube. The decrease in volume is read directly and recorded as the hydrogen content. The amount of CO is found by absorbing the CO_2 obtained from the oxidation of CO by the copper oxide in the caustic potash pipette. This contraction in volume is measured and noted. After the removal of the components just mentioned, a known volume of oxygen is transferred to the slow-combustion pipette. Then a known volume of the residual gas is gradually admitted into this pipette. When the two gases, together, come in contact with the electrically heated filament a slow-burning process ensues and is carried to completion with the complete mixing of the residual gas with the oxygen. After the reaction has cooled to approximately room temperature, the total contraction due to the combustion is determined. The volume of CO_2 , formed in the burning process, is obtained by transferring the residual gas to the caustic potash pipette and measuring the contraction after this absorption has taken place. This is followed by calculations of the volumes of each of the combustible components, which involve considerations of (a) the total number and volume of the combustible components, (b) the total contraction after burning, (c) the total volume of CO_2 formed by the combustion.

The components of a gas mixture are usually removed in the following order: CO_2 , illuminants, O_2 , CO , H_2 , CH_4 , and C_2H_6 .

A typical gas-analysis problem will now be considered in detail.

Example.—A mixture of gases consists of CO , CH_4 , and C_2H_2 . A sample of this gas mixture, measuring 50.0 cc., was transferred to a combustion pipette, 150.0 cc. of oxygen added, and the mixture burned. This is more than enough oxygen for complete combustion of the 50.0 cc. of gas. The gases, after combustion, were allowed to cool, this causing condensation of the water vapor. The volume after cooling measured 122.5 cc. This residual gas was next transferred to the caustic potash pipette; after absorption of CO_2 , the volume measured 57.5 cc. From these data calculate the number of cubic centimeters of each of the gases, CO , CH_4 , and C_2H_2 , in the 50.0 cc. of the original sample.

Let X = number of cubic centimeters of CO in the 50 cc.

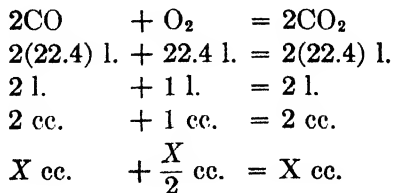
Y = number of cubic centimeters of CH_4 in the 50 cc.

Z = number of cubic centimeters of C_2H_2 in the 50 cc.

Then

$$X + Y + Z = 50 \text{ cc.}$$

The reactions that took place during the combustion are represented by the following equations. These equations also indicate the relative volumes of the gases that combined during the explosion and also the relative volumes of the products formed:



The equation shows that for the complete combustion of 2 cc. of CO , 1 cc. of oxygen is necessary and 2 cc. of CO_2 is formed. Therefore X cc. of CO will require $X/2$ cc. of O_2 for complete combustion. X cc. of CO_2 will be formed.

CH_4	$+ 2\text{O}_2$	$= \text{CO}_2$	$+ 2\text{H}_2\text{O}$
22.4 l.	$+ 2(22.4) \text{ l.}$	$= 22.4 \text{ l.}$	$+ 2(22.4) \text{ l.}$
1 l.	$+ 2 \text{ l.}$	$= 1 \text{ l.}$	$+ 2 \text{ l.}$
1 cc.	$+ 2 \text{ cc.}$	$= 1 \text{ cc.}$	$+ 2 \text{ cc.}$
$Y \text{ cc.}$	$+ 2Y \text{ cc.}$	$= Y \text{ cc.}$	$+ 2Y \text{ cc.}$
$2\text{C}_2\text{H}_2$	$+ 5\text{O}_2$	$= 4\text{CO}_2$	$+ 2\text{H}_2\text{O}$
$2(22.4) \text{ l.}$	$+ 5(22.4) \text{ l.}$	$= 4(22.4) \text{ l.}$	$+ 2(22.4) \text{ l.}$
2 l.	$+ 5 \text{ l.}$	$= 4 \text{ l.}$	$+ 2 \text{ l.}$
2 cc.	$+ 5 \text{ cc.}$	$= 4 \text{ cc.}$	$+ 2 \text{ cc.}$
$Z \text{ cc.}$	$+ \frac{5}{2}Z \text{ cc.}$	$= 2Z \text{ cc.}$	$+ Z \text{ cc.}$

We notice that $X \text{ cc.}$ of CO unites with $X/2 \text{ cc.}$ of O_2 and forms $X \text{ cc.}$ of CO_2 . A mixture of $X \text{ cc.}$ of CO and $X/2 \text{ cc.}$ of O_2 ($3X/2 \text{ cc.}$ total) produced $X \text{ cc.}$ of CO_2 . A contraction of $X/2 \text{ cc.}$ takes place.

In the case of CH_4 , a mixture of $Y \text{ cc.}$ of CH_4 and $2Y \text{ cc.}$ of O_2 forms $Y \text{ cc.}$ of CO_2 and $2Y \text{ cc.}$ of water vapor. After the combustion, the gases were cooled, and the water vapor condensed to liquid water. This volume of liquid water is so small that it can be neglected. The contraction that took place is, therefore, $Y \text{ cc.} + 2Y \text{ cc.} - Y \text{ cc.} = 2Y \text{ cc.}$

In the case of the C_2H_2 , a reaction between $Z \text{ cc.}$ of C_2H_2 and $\frac{5}{2}Z \text{ cc.}$ of O_2 , or $\frac{7}{2}Z \text{ cc.}$ total, forms $2Z \text{ cc.}$ of CO_2 and $Z \text{ cc.}$ of water vapor. This water vapor condenses to a negligible volume of liquid water. The contraction due to combustion and cooling is therefore $\frac{7}{2}Z \text{ cc.} - 2Z \text{ cc.} = \frac{3}{2}Z \text{ cc.}$

The combustion of the three gases mixed with excess O_2 , therefore, causes a contraction of

$$\frac{X}{2} \text{ cc.} + 2Y \text{ cc.} + \frac{3}{2}Z \text{ cc.}$$

By actual measurement the volume before the combustion was 200.0 cc., and after the combustion 122.5 cc., a contraction of 77.5 cc.; *i.e.*,

$$\frac{X}{2} \text{ cc.} + 2Y + \frac{3}{2}Z \text{ cc.} = 77.5 \text{ cc.}$$

The residual volume after the explosion, 122.5 cc., was treated with caustic potash, which absorbed the CO_2 formed from the

combustion of the gases with oxygen. After treatment with KOH, the volume was found to be 57.5 cc. This is a contraction of 65.0 cc. This is the CO_2 formed as one product in the burning of each of the three gases CO, CH_4 , and C_2H_2 . In the burning of the CO, X cc. of CO_2 is formed; in burning the CH_4 , Y cc. of CO_2 is formed; and in the burning of C_2H_2 , $2Z$ cc. is formed; therefore,

$$X + Y + 2Z = 65.0 \text{ cc.}$$

We now have three simultaneous equations in X , Y , and Z . Solving these for X , Y , and Z , which represent the numbers of cubic centimeters of CO, CH_4 , and C_2H_2 , respectively:

$$X + Y + Z = 50.0 \text{ cc.} \quad (1)$$

$$\frac{X}{2} + 2Y + \frac{3}{2}Z = 77.5 \text{ cc.} \quad (2)$$

$$X + Y + 2Z = 65.0 \text{ cc.} \quad (3)$$

Solving these simultaneously,

$$\begin{array}{rcl} X + Y & + & Z = 50.0 \\ X + Y & + & 2Z = 65.0 \\ \hline & & Z = 15.0 \end{array}$$

$$\begin{array}{rcl} X + 4Y & + & 3Z = 155.0 \\ X + Y & + & 2Z = 65.0 \\ \hline 3Y & + & Z = 90.0 \\ & & Z = 15.0 \\ \hline & & 3Y = 75.0 \\ & & Y = 25.0 \end{array}$$

$$\begin{array}{rcl} X + Y & + & Z = 50.0 \\ X + 25.0 & + & 15.0 = 50.0 \\ & & X = 10.0 \end{array}$$

That is,

$$X = \text{number of cubic centimeters of CO} = 10 \text{ cc.}$$

$$Y = \text{number of cubic centimeters of CH}_4 = 25 \text{ cc.}$$

$$Z = \text{number of cubic centimeters of C}_2\text{H}_2 = \frac{15 \text{ cc.}}{50 \text{ cc.}}$$

Problems

648. What volume of air, at S.T.P., is necessary for the complete combustion of (a) 1 ton of coke that contains 98 per cent C, (b) 20 l. of methane, (c) 200 cu. ft. of acetylene, (d) 1,000 l. of carbon monoxide?

Ans. (a) 281,294 cu. ft.; (b) 192.3 l.; (c) 2,403.5 cu. ft.; (d) 2,403 l.

649. Calculate the volume of air, at S.T.P., necessary for the complete combustion of 1,000 cu. ft. of water gas which has the following composition by volume: 1.4 per cent methane, 45.7 per cent carbon monoxide, 46.2 per cent hydrogen, 4.0 per cent nitrogen, 2.4 per cent carbon dioxide.

Ans. 2,340 cu. ft.

650. Calculate the volume of air, at S.T.P., required for the complete combustion of 500 cu. ft. of coal gas that has the following composition: 49.0 per cent hydrogen, 34.8 per cent methane, 4.2 per cent ethylene, 6.0 per cent carbon monoxide, 4.0 per cent nitrogen, 1 per cent carbon dioxide.

Ans. 2,636 cu. ft.

651. How many pounds of carbon dioxide would be produced in Prob. 649?

Ans. 60.77 lb.

652. How many pounds of carbon dioxide would be produced in Prob. 650?

Ans. 30.8 lb.

653. How many cubic feet of carbon dioxide, at S.T.P., is produced in the burning of 1,000 cu. ft. of coal gas that gave the following analysis: 36.8 per cent methane, 47.2 per cent hydrogen, 7.0 per cent carbon monoxide, 4.8 per cent ethylene, 4.0 per cent nitrogen.

Ans. 534 cu. ft.

654. A sample of a gaseous mixture, measuring 100 cc. and containing 40 per cent hydrogen, 10 per cent ethane, 20 per cent methane, 30 per cent carbon monoxide, was mixed with 150 cc. of oxygen in a combustion pipette, and the mixture ignited. Calculate the volume, at S.T.P., of each of the products of combustion.

Ans. 110 cc. H_2O ; 70 cc. CO_2 .

655. A sample of a gaseous mixture, measuring 100 cc., gave on analysis by absorption methods the following data:

Volume after treatment with KOH.....	93.4 cc.
Volume after treatment with fuming H_2SO_4	90.2 cc.
Volume after treatment with alkaline pyrogallol.....	88.3 cc.
Volume after treatment with ammoniacal Cu_2Cl_2	87.8 cc.

Calculate the percentage of CO_2 , C_2H_4 , O_2 , CO, and N_2 in the original mixture.

Ans. 6.6 per cent CO_2 ; 3.2 per cent C_2H_4 ; 1.9 per cent O_2 ; 0.5 per cent CO; 87.8 per cent N_2 .

656. A sample of illuminating gas was analyzed by absorption methods for CO_2 illuminants, O_2 , CO, and H_2 . Calculate the percentage of each of these constituents from the following data:

Volume of sample taken.....	90.0 cc
After treatment with KOH.....	88.0 cc
After fuming H_2SO_4 treatment.....	84.5 cc
After alkaline pyrogallol treatment.....	84.2 cc
After ammoniacal Cu_2Cl_2 treatment.....	48.6 cc
After palladous chloride treatment.....	11.1 cc

Ans. 2.22 per cent CO_2 ; 3.88 per cent illuminants; 0.33 per cent O_2 ; 39.55 per cent CO; 41.66 per cent H_2 .

657. Given 100 cc. of a mixture containing CS_2 vapor and CO. To this 200 cc. of oxygen was added, and the total mixture burned. After the combustion the residual volume measured 245 cc. Calculate (a) the volume of each of the constituents in the original mixture, (b) the volume of oxygen that remained.

Ans. (a) 10 cc. CS_2 , 90 cc. CO; (b) 125 cc. O_2 .

658. Given 90 cc. of mixture of CH_4 and CO. To this 126 cc. of O_2 was added, and the total mixture burned. After the combustion the volume of the cooled gas was found to be 150 cc. Calculate the volume of each of the constituents in the original mixture.

Ans. 14 cc. CH_4 ; 76 cc. CO.

659. A volume of oxygen, measuring 100 cc., was added to a mixture of 94 cc. of H_2 and CO, and the whole was burned in a combustion pipette. The residual volume of the cooled gas after the combustion measured 136 cc. Calculate the percentage composition of the original mixture.

Ans. 11.7 per cent H_2 ; 88.3 per cent CO.

660. A gaseous mixture consisting of CO and C_2H_2 , measuring 40 cc., was mixed with 100 cc. of O_2 and burned. The volume of cooled gas after the combustion measured 105 cc. Calculate the composition of the original mixture.

Ans. 25 cc. CO; 15 cc. C_2H_2 .

661. A gaseous mixture, containing carbon monoxide, methane, and acetylene, measuring 100 cc., was mixed with 400 cc. of oxygen, and the total mixture burned. After cooling, the volume of gas remaining measured 375 cc. This volume was further reduced to 224 cc. by passing the gas through a strong caustic potash solution. Calculate the percentage composition of the original mixture.

Ans. 16.0 per cent CH_4 ; 33.0 per cent CO; 51.0 per cent C_2H_2 .

662. Given 50 cc. of a mixture of H_2 , C_2H_2 , CO. To this was added 80 cc. of oxygen, and the total mixture burned. The volume of the cooled gas after the combustion measured 65 cc. This was reduced to 15 cc. by treatment with KOH solution. Calculate the volume of each of the three gases in the original mixture.

Ans. 20 cc. H_2 ; 20 cc. C_2H_2 ; 10 cc. CO.

663. Given 30 cc. of a mixture of CO, CH_4 , and C_2H_2 to which 65 cc. of O_2 was added, and the total mixture burned. The volume of cooled gas after the combustion measured 55 cc. This was further reduced to

15 cc. by absorption of the CO_2 by KOH solution. Calculate the volume of each gas in the original mixture.

Ans. 10 cc. CO ; 10 cc. CH_4 ; 10 cc. C_2H_2 .

664. Given 100 cc. of a mixture of CH_4 , CO , and N_2 . To this was added 100 cc. of oxygen, and the total mixture burned. Volume of cooled gas after the combustion was 125 cc. By absorption with KOH solution the volume was further reduced to 65 cc. Calculate the volume of each of the gases in the original mixture.

Ans. 30 cc. CH_4 ; 30 cc. CO ; 40 cc. N_2 .

665. Calculate the volume of CO and C_2H_2 in a mixture of the two gases from the following:

Volume of mixture taken.....	40.0 cc.
Volume of O_2 added.....	100.0 cc.
Volume after combustion (with cooling).....	96.0 cc.

Ans. 16 cc. CO ; 24 cc. C_2H_2 .

666. Given a mixture of 50 cc. of C_2H_4 and C_2H_2 to which 150 cc. of oxygen was added, and the total mixture burned. The volume of cooled gas after the combustion measured 112.5 cc. Calculate the volume of each gas in the original mixture.

Ans. 25 cc. C_2H_4 ; 25 cc. C_2H_2 .

667. Given 65.0 cc. of a mixture of CH_4 and C_2H_2 to which 144.5 cc. of O_2 was added, and the total mixture burned in a combustion pipette. The residual volume after the combustion, without cooling, measured 195.0 cc. When the products of combustion were passed through calcium chloride tubes, to remove the water vapor, the final volume measured 94.0 cc. Calculate (a) the volume of each of the constituents in the original mixture, (b) the volume of water vapor produced.

Ans. (a) 36 cc. CH_4 , 29 cc. C_2H_2 ; (b) 101 cc. water vapor.

668. Given a mixture of CH_4 , C_2H_2 , and C_3H_8 . Calculate the volume of each gas from the following:

Volume of gas taken.....	25.0 cc.
Volume of O_2 added.....	75.0 cc.
Volume of cooled gas after combustion.....	49.5 cc.
Volume after CO_2 absorption.....	17.5 cc.

Ans. 20 cc. CH_4 ; 3 cc. C_2H_2 ; 2 cc. C_3H_8 .

669. Given a mixture of CO , CH_4 , C_2H_4 , and N_2 . Calculate the volume of each gas from the following data:

Volume of gas taken.....	30.0 cc.
Volume of O_2 added.....	50.0 cc.
Volume after combustion (without cooling).....	75.0 cc.
Volume after removing the water vapor by CaCl_2	45.0 cc.
Volume after absorption of CO_2 by KOH	15.0 cc.

Ans. 10 cc. CO ; 10 cc. CH_4 ; 5 cc. C_2H_4 ; 5 cc. N_2 .

670. Calculate the volume of CO , H_2 , C_2H_4 , and N_2 from the following data:

Volume of sample taken.....	80.0 cc.
Volume of O_2 added.....	100.0 cc.
Residual volume after combustion (without cooling).....	160.0 cc.
Volume after removal of water vapor by CaCl_2	100.0 cc.
Volume after removal of CO_2 by KOH	40.0 cc.

Ans. 20 cc. CO ; 20 cc. H_2 ; 20 cc. C_2H_4 ; 20 cc. N_2 .

671. A gaseous mixture consisting of CO_2 , CO , H_2 , and N_2 , upon analysis, gave the following data:

Volume of sample taken.....	100.0 cc.
Volume after KOH treatment.....	93.3 cc.
Volume after ammoniacal Cu_2Cl_2 treatment.....	72.9 cc.

Fifty cubic centimeters of this residual volume (*i.e.*, of the 72.9 cc.) was taken, and 50 cc. of oxygen added, and this mixture burned (assume a constant temperature of 100°C .). The residual volume after the combustion measured 80 cc. Calculate the percentages of the constituents in the original mixture.

Ans. 6.7 per cent CO_2 ; 20.4 per cent CO ; 58.32 per cent H_2 ;
14.58 per cent N_2 .

672. A 10-cc. sample of natural gas is burned with 90.0 cc. of oxygen.

Volume after combustion.....	76.4
Volume after KOH	58.0

Determine the percentage of ethane, methane, and nitrogen in this gas.

Ans. Ethane, 88.0 per cent; methane, 8.0 per cent.

673. A 100.0-cc. sample of coke-oven gas analyzed in a Burrell gas-analysis apparatus gave the following results:

Volume after KOH	98.3 cc.
Volume after fuming sulfuric acid.....	95.2 cc.
Volume after alkaline pyrogallol.....	94.8 cc.
Volume after copper oxide.....	35.9 cc.
Volume after KOH	31.1 cc.

Ten cubic centimeters of residual gas was burned with 80.0 cc. of oxygen.

Volume after combustion.....	72.9 cc.
Volume after KOH	63.6 cc.

Calculate the percentage of the constituents in the gas.

Ans. 1.7 per cent CO_2 ; 3.1 per cent illuminants; 0.4 per cent O_2 ;
58.9 per cent H_2 ; 4.8 per cent CO ; 22.7 per cent CH_4 ; 3.1 per cent
 C_2H_6 ; 5.3 per cent N_2 .

674. A sample of Blau gas gave the following analysis:

Volume of sample taken.....	100.0 cc.
Volume after KOH.....	100.0 cc.
Volume after fuming sulfuric acid.....	48.1 cc.
Volume after pyrogallol.....	48.1 cc.
Volume after ammoniacal Cu_2Cl_2	48.0 cc.

Twelve cubic centimeters of residual gas burned with 88.0 cc. of oxygen.

Volume after combustion.....	75.9 cc.
Volume after KOH.....	64.9 cc.

Calculate the percentage composition of this gas.

Ans. 51.9 per cent illuminants; 0.1 per cent CO; 2.8 per cent H_2 ;
44.0 per cent CH_4 .

675. A 100-cc. sample of producer gas gave the following results in a Burrell apparatus:

Volume after KOH.....	90.2 cc.
Volume after fuming sulfuric acid.....	90.0 cc.
Volume after pyrogallol.....	89.9 cc.
Volume after copper oxide.....	77.0 cc.
Volume after KOH.....	58.7 cc.

Ten cubic centimeters of residual gas burned with 90.0 cc. of oxygen.

Volume after combustion.....	99.0 cc.
Volume after KOH.....	98.5 cc.

Determine the percentage composition of this gas.

Ans. CO_2 , 9.8 per cent; illuminants, 0.2 per cent; O_2 , 0.1 per cent;
 H_2 , 12.9 per cent; CO, 18.3 per cent; CH_4 , 3.1 per cent.

Additional Problems without Answers, for Quizzes

676. Calculate the percentage composition of a gaseous mixture of CH_4 and C_3H_8 from the following data:

Volume of gas taken.....	30.0 cc.
Volume of O_2 added.....	105.0 cc.
Volume of cooled gas after combustion.....	60.0 cc.

677. Given 75.0 cc. of a mixture containing CH_4 , CO, and C_2H_2 . To this was added 125.0 cc. of oxygen, and the whole mixture burned. The volume of the cooled gas after combustion measured 132.0 cc., and this was further reduced by absorption of the CO_2 , by strong KOH solution, to 52.0 cc. Calculate (a) the volume of each of the gases in the original mixture; (b) the volume of oxygen that was not consumed in the explosion.

- 678.** Calculate the volume of each gas in a mixture of H_2 , CO , and N_2 from the following:

Volume of sample taken.....	50.0 cc.
Volume of O_2 added.....	20.0 cc.
Volume of cooled gas after combustion.....	44.9 cc.
Volume after removal of CO_2	32.5 cc.

- 679.** Given 30 cc. of a mixture of CH_4 , C_2H_4 , and N_2 . To this was added 60.0 cc. of oxygen, and the total mixture burned. Residual volume of cooled gas after combustion measured 50.0 cc. After removal of CO_2 the volume was 20.0 cc. Calculate the percentage composition of the original mixture.

- 680.** Given 45 cc. of a mixture of CO , CH_4 , and C_2H_2 to which 97.5 cc. of O_2 was added, and the total mixture burned. Volume of cooled gas after the combustion measured 82.5 cc. This was further reduced to 22.5 cc. by absorption of the CO_2 by KOH solution. Calculate the volume of each gas in the original mixture.

- 681.** Given a mixture of CH_4 , C_2H_2 , and C_3H_8 . Calculate the percentage composition of the original mixture from the following data:

Volume of gas taken.....	100.0 cc.
Volume of O_2 added.....	300.0 cc.
Volume of cooled gas after combustion.....	198.0 cc.
Volume after CO_2 absorption.....	70.0 cc.

- 682.** Given 25 cc. of a mixture of H_2 , C_2H_2 , and CO . To this was added 40 cc. of O_2 , and the total mixture burned. The volume of the cooled gas after the combustion measured 32.5 cc. This was reduced to 7.5 cc. by treatment with KOH solution. Calculate the volume of each of the three gases in the original mixture.

- 683.** A sample of illuminating gas on analysis gave the following data:

Volume of sample taken.....	100.0 cc.
Volume after removal of CO_2	95.8 cc.
Volume after removal of illuminants.....	86.9 cc.

Ten cubic centimeters of the residual gas containing H_2 , CH_4 , CO , and N_2 was burned with 20.0 cc. of O_2 . The volume after combustion measured 22.3 cc.; after removing CO_2 , 18.6 cc.; and after removing excess oxygen, 3.5 cc. Calculate the percentage composition of the gas.

- 684.** A sample of gas measuring 90.4 cc. was taken. After passing through KOH solution, the volume was reduced to 90.2 cc. After passing through fuming sulfuric acid, the volume was reduced to 88.0 cc. This volume was then exposed to the action of phosphorus, and there was no further reduction in volume. Of the residual 88 cc. of gas, 40.8 cc. was then passed over heated CuO . The volume after cooling was found to be 38.0 cc. On passing this gas into KOH solution the volume was further reduced to 6.0 cc. Calculate the percentage composition of the gas.

- 685.** Given 100 cc. of illuminating gas of the following composition: 4.2 per cent CO_2 , 8.9 per cent C_2H_6 , 24.4 per cent H_2 , 9.6 per cent CH_4 , 22.6 per cent CO , 30.3 per cent N_2 . Calculate the total volume of products at 100°C . obtained by burning this gas, using 10 per cent excess air.
- 686.** Kerosene, which is really a mixture of hydrocarbons from C_9H_{20} to $\text{C}_{17}\text{H}_{36}$ may be considered as $\text{C}_{14}\text{H}_{30}$. If a coal-oil stove burns 300 g. of kerosene per hour, calculate (a) the number of liters of oxygen consumed per hour by this stove; (b) the percentage of oxygen left in the air in a room 7 by 10 by 10 ft. after the stove had been burning for 3 hr., assuming that no fresh air was admitted to the room.
- 687.** A small oil stove, used for domestic heating, burns 400 g. of kerosene per hour. Considering kerosene as $\text{C}_{14}\text{H}_{30}$, calculate (a) the volume of oxygen consumed per hour by this stove; (b) the volume of CO_2 and water vapor formed per hour; (c) the volume of oxygen remaining in a room 7 by 10 by 12 ft. after the stove had been burning for 3 hr., assuming that no fresh air is added to the room.
- 688.** A 100.0-cc. sample of coke-oven gas, analyzed in a Burrell gas-analysis apparatus, gave the following results:

Volume after KOH.....	97.7 cc.
Volume after fuming sulfuric acid.....	93.7 cc.
Volume after alkaline pyrogallol.....	93.4 cc.
Volume after copper oxide.....	37.8 cc.
Volume after KOH.....	29.6 cc.

Ten cubic centimeters of residual gas was burned with 90.0 cc. of oxygen.

Volume after combustion.....	83.4 cc.
Volume after KOH.....	74.5 cc.

Calculate the percentage of the constituents in the gas.

CHAPTER XII

OUTLINE

Heat is evolved or absorbed when a chemical reaction takes place.

The calorific power of a substance is the heat evolved (calories) during the combustion of a unit weight of a substance. In the case of gases it is often considered as the heat evolved by the combustion of a unit volume of the gas.

Calorific power of some familiar substances.

Solution of an example. Calorific power of a sample of coal.

Calorific intensity. The highest theoretical temperature to which the products of a combustion are raised by the heat evolved.

Specific heat of a gas. The quantity of heat (calories) required to raise the unit volume (usually 1 l.) of the gas through 1°C .

Specific heats of N_2 , H_2 , O_2 , CO , CO_2 , H_2O vapor.

Solution of an example. The temperature of the flame of hydrogen when burning (a) in oxygen, (b) in 20 per cent excess air.

CALORIFIC POWER AND CALORIFIC INTENSITY

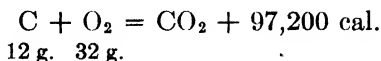
When a chemical reaction takes place, the original substances disappear, and new substances are formed. Coincident with this change occurs a transformation of energy, with the result that the chemical reaction is accompanied by the evolution or absorption of heat; in other words, the temperature of the products of the reaction becomes higher or lower than that of the original substances.

A reaction during which heat is evolved is known as an **exothermic reaction**; and one in which heat is absorbed an **endothermic reaction**.

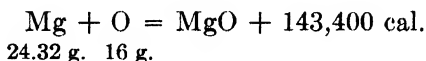
In considering the calorific power of substances, we shall deal exclusively with exothermic reactions of a type included under the term **combustion**.

By the combustion of a substance we commonly understand that it burns in air or oxygen and in so doing emits light and heat. Such a phenomenon implies a chemical reaction and can be expressed by an equation.

When a piece of charcoal burns in the air, the carbon unites with oxygen to form carbon monoxide or carbon dioxide, depending on whether there is a deficiency or an excess of air. At the same time heat is evolved. The quantity of heat evolved when 1 gram-mol (12 g.) of carbon unites with 1 gram-mol (32 g.) of oxygen is 97,200 cal. This is indicated by the equation



Similarly, when a piece of magnesium ribbon burns in the air, the quantity of heat evolved in the reaction is represented by the equation



When iron and sulfur are heated together under the proper conditions, they combine with the evolution of light and heat as represented by the equation



The heat evolved in these various reactions can be measured by carrying out the chemical change in an instrument known as a "calorimeter." The heat evolved is expressed in **calories**, or *British thermal units* (B.t.u.).

The calorie (cal.) is the quantity of heat necessary to raise the temperature of one gram of water one degree centigrade, or, more exactly, from 15°C. to 16°C. The large, or kilogram, calorie (Cal.) is equal to 1,000 cal.

The British thermal unit is the quantity of heat necessary to raise the temperature of one pound of water one degree Fahrenheit.

In a great many cases it is more convenient, though not so accurate, to arrive at the heat evolved in a combustion reaction by calculating from previously determined data instead of making an actual calorimetric test. In order to do this, we have recourse to what are known as the calorific powers, or the heats of combustion of substances. These have previously been determined by careful experiment.

The **calorific power**, or heating value, of a substance is the heat evolved by the combustion of a unit mass of the substance. It is usually expressed in calories per gram-mol, calories per kilogram-mol, or B.t.u. per pound. This number of units is a constant for any given substance, irrespective of the manner in which the combustion is carried on, so long as it is complete; for example, the calorific power of a substance is the same whether the substance is burned in air or in pure oxygen.

The following table gives the calorific power in calories per gram-mol of various substances. For instance,

$$(C, O_2) \quad 12 + 32 = 44 \quad 97,200$$

simply means that when 12 g. of carbon unites with 32 g. of oxygen, 44 g. of carbon dioxide is formed, and at the same time 97,200 calories of heat is evolved. Hence, when carbon burns to carbon dioxide, the heat evolved amounts to 97,200 cal. per gram-mol of carbon, or 97,200 Cal. per kilogram-mol. The calorific power, per gram of carbon, would be

$$\frac{97,200}{12} = 8,100 \text{ cal.}$$

TABLE XI.—CALORIFIC POWER OF SOME SUBSTANCES

Substance	Molecular weights (approx.)	Heat evolved (cal. per mol)
C, O ₂ ¹	12 + 32 = 44	97,200
H ₂ , O	2 + 16 = 18	68,977 liquid ² 58,060 gas
S, O ₂	32 + 32 = 64	69,260
P ₂ , O ₅	62 + 80 = 142	365,300
CO, O	28 + 16 = 44	68,040
Zn, O	65 + 16 = 81	84,800
Mn, O	55 + 16 = 71	90,900
Si, O ₂	28 + 32 = 60	196,000
Sn, O ₂	118 + 32 = 150	141,300
Fe ₂ , O ₃	112 + 48 = 160	195,600

¹ See Richards, "Metallurgical Calculations," p. 19.

² In ordinary work the moisture formed by the combustion of hydrogen passes off as vapor, but if it be condensed, as is the case in calorific measurements, then taking the products cold, the heat of condensation of water (606.5 cal. per gram of water) is liberated and the total heat evolved = 58,060 + (18 × 606.5) = 68,977.

TABLE XII.—HEATS OF FORMATION OF SOME OXIDES

H ₂ , O (vapor).....	28,690 cal./g. of H
C, O.....	2,430 cal./g. of C
C, O ₂	8,100 cal./g. of C
S, O ₂	2,212 cal./g. of S
P ₂ , O ₅	5,912 cal./g. of P

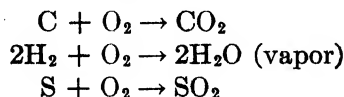
The calorific power of gases is usually expressed as calories per liter or calories per cubic meter, and it is advisable in gas calculations to use the calorific power per unit volume rather than the calorific power per unit weight, since in most cases it is more desirable to ascertain the volumes of gases than their weights.

Example.—Since in engineering work the only kind of combustion considered for the production of heat is the combination of various kinds of fuel with the oxygen of the air, let us calculate the heat evolved by the combustion of 1 g. of coal, the analysis of which is

	PER CENT
Carbon.....	72.0
Hydrogen.....	5.0
Oxygen.....	8.0
Nitrogen.....	1.0
Sulfur.....	0.8
Ash.....	13.2

In general, the calorific power of a *compound* will not be the sum of the calorific powers of the elements of which it is composed. This is due to the fact that some of the heat is utilized in undoing the work of combination of the compounds.

In this example the carbon, hydrogen, and sulfur are the combustible constituents; then



The nitrogen and ash do not enter into the calculations, since they do not combine with oxygen under these conditions. The nitrogen passes off as such with the products of combustion, and the ash remains as a residue.

Since C = 72.0 per cent, we have 0.72 g. of C in each 1 g. of coal.

1 gram-mol of C (12 g.) in burning to CO_2 evolves 97,200 cal. of heat, or 8,100 cal. per gram of C.

The heat evolved by 0.72 g. of C in the 1 g. of coal is $0.72 \times 8,100 = 5,832$ cal.

The hydrogen unites with oxygen to form water vapor. In the case of fuel we assume that all the oxygen shown to be present by analysis is already combined with part of the hydrogen, thus leaving only a portion of the hydrogen to unite with the oxygen of the air. And it is only this portion of the hydrogen that evolves heat when the fuel is burned. The first step, then, is to calculate the portion of hydrogen already combined with the oxygen in the coal.

From analysis we know that in water

16 g. of oxygen is combined with 2.016 g. of hydrogen.

Or

1 g. of oxygen is combined with $2.016/16$ g. of hydrogen.

Analysis shows 1 g. of the coal to contain 0.08 g. of oxygen. Therefore the hydrogen combined with this is

$$0.08 \times \frac{2.016}{16.00} = 0.01 \text{ g. of hydrogen}$$

The hydrogen left over, or available hydrogen, as it is called, is

$$0.05 \text{ g.} - 0.01 \text{ g.} = 0.04 \text{ g.}$$

1 gram-mol of H_2 (2.016 g.) in forming H_2O vapor evolves 28,690 cal. per gram of H. (See Table XII.)

The heat evolved by 0.04 g. of available hydrogen is $0.04 \times 28,690 = 1,147$ cal.

1 gram-mol of S (32.06 g.) in forming SO_2 evolves 2,212 cal. per gram of S.

The heat evolved by 0.008 g. of S in 1 g. of coal is $0.008 \times 2,212 = 17.7$ cal.

The total heat evolved by the constituents carbon, hydrogen, and sulfur is

	CALORIES
Heat from carbon.....	5,832
Heat from available hydrogen.....	1,147
Heat from sulfur.....	17.7
Total heat evolved per gram of coal.....	6,996.7

TABLE XIII.—CALORIFIC POWER OF SOME GASES

		cal./l., or Cal./cu. m.	B.t.u./cu. ft.
Hydrogen.....	H ₂	2,582	290
Carbon monoxide.....	CO	3,034	341
Methane.....	CH ₄	8,590	966
Ethylene.....	C ₂ H ₄	14,240	1,602
Ethane.....	C ₂ H ₆	15,155	1,702
Acetylene.....	C ₂ H ₂	13,590	1,528
Benzene.....	C ₆ H ₆	33,560	3,775

NOTE: 1 B.t.u./cu. ft. = 8.9 kg.-cal. per cubic meter.

MAXIMUM THEORETICAL TEMPERATURE

The maximum theoretical temperature (starting from 0°C.) to which the products of combustion of a substance are raised by the heat liberated by the combustion is sometimes called the **calorific intensity**.

When a substance burns, definite weights and volumes of combustion products are formed, and a definite amount of heat is liberated. This heat raises the temperature of the products of combustion. In order to calculate what this temperature will be in any given case, we must first calculate the volumes¹ or weights of the products, together with the heat evolved; knowing the amount of heat necessary to raise a unit weight or volume of the products of combustion one degree centigrade, the final temperature to which they are raised is not difficult to calculate.

The number of heats units expressed in calories, required to raise the temperature of a certain amount of any substance one degree centigrade, is called the specific heat-capacity, or **specific heat**, of the substance. In the case of solids the specific heat is expressed as calories required to raise the temperature of one gram of the substance one degree centigrade. In the case of gases, however, it is more convenient to express it as calories required to raise one liter of the gas one degree centigrade.

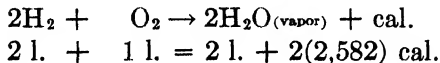
¹ The composition of gases is usually expressed as percentage by volume, and it must be remembered that 1 gram-mol of any gas, at S.T.P., occupies 22.4 l. This enables us to calculate the weight of a liter of any gas.

The following are the mean specific heats of gases between 0° and $t^{\circ}\text{C}$. They are given in calories per liter per degree centigrade.

CALORIES PER LITER PER DEGREE CENTIGRADE	
Nitrogen	} (0.302 + 0.000022t)
Hydrogen	
Oxygen	
Air	
Carbon monoxide	} (0.406 + 0.00009t)
CO ₂ and SO ₂	
H ₂ O (vapor).....	
 (0.373 + 0.00005t)

Example.—In order to show the application of the foregoing remarks let us calculate the maximum theoretical temperature reached when hydrogen is burned (a) in oxygen, (b) in 20 per cent excess air.

(a) The burning of hydrogen in oxygen involves the following relations:



or

$$1 \text{ l.} + 0.5 \text{ l.} = 1 \text{ l.} + 2,582 \text{ cal.}$$

Disregarding the heat utilized in raising the temperature of surrounding bodies, we may consider that, theoretically, all the heat produced by the burning of a substance is utilized in raising the temperature of the products of combustion. In the case under consideration the 2,582 cal. is used in raising the temperature of the 1 l. of water vapor produced.

The heat required to raise 1 l. of water vapor 1°C . is $(0.373 + 0.00005t)$ cal.

The heat evolved is 2,582 cal./l. of water vapor.

Assuming that the total heat available in the combustion is equal to the heat taken up by the products of combustion immediately after the reaction, the temperature rise will be

$$t = \frac{\text{cal.}}{V \times \text{sp. ht.}}$$

where t = temperature in degree centigrade.

cal. = number of calories available.

V = volume of gases.

sp. ht. = specific heat of gases.

When 1 l. of hydrogen burns in oxygen, the temperature rise $t^{\circ}\text{C}$. will therefore be

$$\frac{2,582}{(0.373 + 0.00005t)} = t^{\circ}\text{C}.$$

$$2,582 = 0.373t + 0.00005t^2$$

$$0.00005t^2 + 0.373t - 2582 = 0$$

Multiply by 10,000:

$$0.5t^2 + 3730t - 25,820,000 = 0$$

$$t = \frac{-3,730 + \sqrt{(3,730)^2 + 4(0.5)(25,820,000)}}{2 \times 0.5}$$

$$t = 4366^{\circ}\text{C}.$$

If we start from 0°C ., the maximum theoretical temperature is 4366°C .

(b) When hydrogen is burned in excess air, the products of combustion will consist of water vapor and excess air ($\text{O}_2 + \text{N}_2$).

The heat produced per liter of hydrogen is the same as in part (a), *viz.*, 2,582 cal./l., but the heat liberated raises the temperature of the water vapor and also the excess air. It is necessary to determine this amount of excess O_2 and N_2 .

The volume of oxygen required by 1 l. of hydrogen = 0.5 l.

The composition of air by volume is 79.1 per cent of nitrogen and 20.9 per cent of oxygen; *i.e.*,

20.9 l. of O_2 in 100 l. of air

$$0.5 \text{ l. of } \text{O}_2 \text{ in } 0.5 \times \frac{100}{20.9} = 2.39 \text{ l. of air}$$

Since 20 per cent excess air is used, $0.2 \times 2.39 \text{ l.} = 0.478 \text{ l.}$ of excess air.

$$2.39 \text{ l.} + 0.478 \text{ l.} = 2.868 \text{ l. of air (O}_2 \text{ and N}_2\text{)}$$

But 0.5 l. of oxygen is used in the combustion of 1 l. of hydrogen; then

2.868 l. - 0.5 l. = 2.368 l. of ($O_2 + N_2$) will absorb heat as well as the 1 l. of water vapor.

The heat necessary to raise 1 l. of water vapor $1^\circ C.$ is $(0.373 + 0.00005t)$.

The heat necessary to raise 2.368 l. of ($O_2 + N_2$) $1^\circ C.$ is $2.368(0.302 + 0.000022t)$.

The heat required to raise the products of the reaction $1^\circ C.$:

$$\begin{aligned} 1 \text{ l. of water vapor} &= 0.373 + 0.00005t \\ 2.368 \text{ l. of air } (O_2 + N_2) &= 0.715 + 0.00005t \\ \text{Both substances} &= 1.088 + 0.00010t \end{aligned}$$

Total heat liberated = 2,582 cal. per liter of hydrogen.

The temperature rise t , in degrees centigrade, will be

$$\begin{aligned} \frac{2,582}{(1.088 + 0.0001t)} &= t^\circ C. \\ 2,582 &= 1.088t + 0.0001t^2 \end{aligned}$$

Multiply by 10,000:

$$\begin{aligned} t^2 + 10,880t - 25,820,000 &= 0 \\ t &= 2004^\circ C. \end{aligned}$$

Problems

689. Calculate the calorific power of a producer gas that gave the following analysis: 6.0 per cent CO_2 ; 22.0 per cent CO ; 12.0 per cent H_2 ; 60.0 per cent N_2 . *Ans.* 977 cal./l.
690. Calculate the calorific power of a natural gas that gave the following chemical analysis: 0.6 per cent CO ; 0.2 per cent CO_2 ; 1.8 per cent H_2 ; 93.5 per cent CH_4 ; 3.4 per cent N_2 . *Ans.* 8096 cal./l.
691. Calculate the calorific power of water gas that contains 1.4 per cent CH_4 ; 45.5 per cent CO ; 47.4 per cent H_2 ; 2.0 per cent CO_2 ; 4.0 per cent N_2 . *Ans.* 2725 cal./l.
692. Calculate the calorific power of anthracite coal of the following analysis: 93.5 per cent C ; 3.0 per cent moisture; 3.5 per cent ash. *Ans.* 7574 cal./g.
693. Calculate the calorific power of bituminous coal that contained by analysis: 74.0 per cent C ; 1.52 per cent S ; 5.46 per cent H_2 ; 7.92 per cent ash; 12.01 per cent moisture. *Ans.* 7594 cal./g.
694. Calculate the calorific power of a powdered coal used in a rotary cement kiln. This coal gave the following analysis: 2.17 per cent moisture; 85.00 per cent carbon; 8.83 per cent ash; 4.12 per cent S . *Ans.* 6976 cal./g.

695. Calculate the calorific power of an oil gas that has the following composition: 30.0 per cent H_2 ; 49.5 per cent CH_4 ; 15.0 per cent C_2H_4 ; 3.5 per cent N_2 . *Ans.* 7172 cal./l.
696. A carbureted water gas has the following percentage composition: 29.8 per cent CO; 40.0 per cent H_2 ; 17.0 per cent CH_4 ; 7.8 per cent C_2H_4 ; 3.8 per cent N_2 ; 1.5 per cent CO_2 . Calculate the calorific power of this gas. *Ans.* 4508 cal./l.
697. Calculate the calorific power of wood that has the following analysis: 18.0 per cent H_2O ; 81.0 per cent C; 1.0 per cent ash. *Ans.* 6561 cal./g.
698. Calculate the calorific power of coke that has the following percentage composition: 90.2 per cent C; 2.4 per cent H_2O ; 7.4 per cent ash. *Ans.* 7306 cal./g.
699. Calculate the maximum theoretical temperature obtained when carbon monoxide is burned in oxygen. *Ans.* 3972°C.
700. Calculate the maximum theoretical temperature obtained when carbon monoxide is burned in air. *Ans.* 2350°C.
701. Methane is burned in air. Calculate the maximum theoretical temperature reached. *Ans.* 2125°C.
702. Calculate the theoretical temperature of the oxyhydrogen blowtorch. *Ans.* 4366°C.
703. Calculate the calorific intensity of hydrogen when burned in air. *Ans.* 2250°C.
704. Calculate the maximum theoretical temperature of combustion of acetylene in air. *Ans.* 2420°C.
705. Calculate the theoretical temperature of the oxyacetylene blowtorch. *Ans.* 5530°C.
706. Calculate the calorific intensity when pure carbon is burned in air. *Ans.* 3036°C.
707. Calculate the maximum theoretical temperature of combustion of ethylene when burned in air. *Ans.* 2295°C.
708. Calculate the calorific intensity of benzol when burned in air. *Ans.* 2230°C.
709. C_6H_6 is burned in a blast lamp with 10 per cent excess air. Calculate the maximum theoretical temperature attained. *Ans.* 2085°C.
710. Calculate the temperature of the flame of an air-blast lamp that burns carbon monoxide and uses 25 per cent excess air over that needed for combustion. *Ans.* 2090°C.
711. Calculate the maximum theoretical temperature that can be reached in a Bunsen burner using gas of the composition: carbon monoxide, 30.0 per cent; methane, 3.5 per cent; nitrogen, 60.0 per cent; hydrogen, 6.5 per cent; no excess of air. *Ans.* 1765°C.
712. Calculate the maximum theoretical temperature of combustion of a gas of the following composition: carbon monoxide, 60 per cent; methane, 20 per cent; hydrogen, 20 per cent, when burned (a) in air, (b) in oxygen. *Ans.* (a) 2220 °C.; (b) 4185°C.

Additional Problems for Quizzes, without Answers

- 713.** Acetylene is burned in a blast lamp using 20 per cent excess air. Calculate the maximum theoretical temperature of combustion under these conditions.
- 714.** Calculate the maximum theoretical temperature of combustion when ethyl alcohol, C_2H_5OH , is burned in air. Calorific power of C_2H_5OH is 293,680 cal. per mol.
- 715.** Calculate the temperature of the flame of an oxyacetylene blowtorch that uses 15 per cent excess oxygen over that needed for complete combustion.
- 716.** Calculate the maximum theoretical temperature of combustion of ethane when burned in air.
- 717.** Calculate the maximum theoretical temperature of combustion when methol (methyl alcohol), CH_3OH , is burned in air. Calorific power of CH_3OH is 148,270 cal. per mol.

CHAPTER XIII

OUTLINE

ELECTROLYSIS

Electrodes, anode, cathode, anion, cation.

The electric current directs the motion of the charged particles (ions) present in the solution.

Faraday's Laws. The amount of an ion liberated in a given length of time is proportional to the strength of the current.

Equal quantities of current liberate amounts of various ions which are proportional to the chemical equivalents of these ions.

One ampere in 1 sec. will liberate 0.001118 g. of silver, or 0.00001037 g. of hydrogen (S.T.P.).

96,494 amp.-sec. (coulombs) is required to liberate one gram-equivalent of a substance at the electrodes.

POWER

$P = EI$. P is in watts, E in volts, I in amperes.

RESISTANCE

The ohm. The flow of an electric current through a wire is analogous to the flow of water through a pipe.

Specific resistance. The resistance of a centimeter cube of the material.

$R = KL/S$, where K is the specific resistance, L is the length of solution between electrodes, and S the cross section of the solution in square centimeters.

ELECTROLYSIS

If two sheets of copper are suspended in a solution of copper sulfate and the sheets are connected to the terminals of a battery or other source of electric current, the one copper sheet will slowly dissolve, and at the same time metallic copper will be deposited on the second sheet. Chemical action is taking place at the surface of the two copper sheets. The chemical action thus produced by the electric current is called **electrolysis**. The two copper sheets are called **electrodes**: the one that dissolves and through which the current enters the cell is called the positive

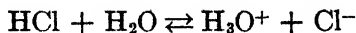
electrode, or **anode**; the one on which the copper deposits and through which the current leaves the cell is called the negative electrode, or **cathode**.

As a second example of simple electrolysis we may take the electrolytic decomposition of a solution of hydrochloric acid, using carbon electrodes. In this case, hydrogen is liberated at the cathode, and chlorine at the anode, the net result of the action of the current being the separation of the molecule of the dissolved substances into two parts. That part of the molecule which goes to the cathode (hydrogen in this case) is called the **cation**; that part which goes to the anode (chlorine in this case) is called the **anion**. In all salts and bases the metal constitutes the cation; the acid radical (halogen, hydroxyl group, etc.) constitutes the anion. In the case of sodium nitrate, NaNO_3 , for instance, Na^+ is the cation, and NO_3^- the anion.

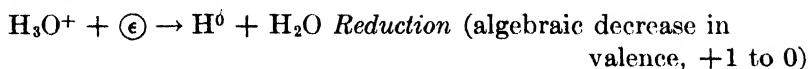
The mechanism of the electrolysis of an aqueous solution of hydrochloric acid may be considered somewhat along these more modern lines of thought. In this acid solution there are hydrogen ions or, more truly, hydronium ions (H_3O^+), chloride ions (Cl^-), and a small concentration of hydroxyl ions (OH^-), which are present because of the slight ionization of water. When a difference of potential exists between the electrodes, ionic migration takes place. The cation, H_3O^+ , travels to the cathode, where it acquires an electron from the electrode, and in so doing becomes reduced to hydrogen atoms and H_2O . These hydrogen atoms in turn form molecules of hydrogen gas that escape from the cathode compartment of the cell. Simultaneously with this reaction the chloride ion, Cl^- , migrates to the anode where it loses an electron, thereby becoming oxidized to free chlorine. These chlorine atoms form molecules of chlorine gas that escape from the anode compartment of the cell.

The conclusion can be drawn that during electrolysis of aqueous solutions of acids, bases, and salts, *reduction* (gain of electrons) occurs at the *cathode*, and *oxidation* (loss of electrons) takes place at the *anode*. The following electrode reactions will summarize the foregoing statements:

Ionization of HCl :



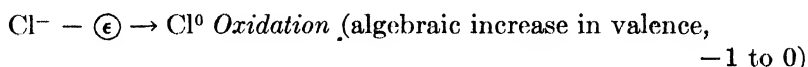
Cathode reaction:



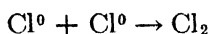
Escaping at the cathode:



Anode reaction:



Escaping at the anode:



It is generally accepted that when a salt, *e.g.*, copper sulfate, is dissolved in water, it immediately breaks up (dissociates) to some extent into charged particles. These charged particles are called **ions**. The solution then will contain ions of Cu and ions of SO_4 together with some undissociated molecules of copper sulfate. The Cu ion (cation) will carry a positive charge of electricity, whereas the SO_4 ion (anion) will carry a negative charge.

In general, all acids, bases, and salts, when dissolved in water, exhibit this same behavior of splitting up into charged particles.

This assumption was first made by Clausius in 1857. He observed that Cu was liberated at the cathode and SO_4 at the anode during electrolysis and reasoned that if this breaking up of the molecule of CuSO_4 were due to the electric current, then for each substance there would be a definite minimum electromotive force (voltage) necessary to decompose the compound. When, however, he electrolyzed a solution of silver nitrate, using silver electrodes, even the smallest voltage forced through the cell a current sufficient to cause electrolysis. He therefore concluded that the current does not exert any disruptive action on the molecules but simply directs the motion of the ions that have already been formed by the act of solution. Consequently, if a difference of potential is established between the electrodes, the positively charged ions (cations) will be attracted to the negative electrode (cathode); whereas the negatively charged ions (anions) will

travel toward the positive electrode (anode). When the ions reach their respective electrodes, they give up their electric charges; they then cease to be ions and exhibit the ordinary chemical properties of the elements liberated.

The quantitative relations between the current strength and the amount of the various ions liberated at the electrodes were determined experimentally by Michael Faraday and may be stated in the form of two laws as follows:

I. *The amount of an ion liberated at an electrode in a given length of time is proportional to the strength of the current.*

II. *The same quantity of current when passed through different electrolytes liberates amounts of the ions that are proportional to the chemical equivalents of the ions.*

Faraday passed the same current, for the same length of time, through solutions of cupric sulfate, silver nitrate, dilute sulfuric acid, cuprous sulfate, zinc sulfate and several others by connecting the solutions in series. He measured the amount of the ions liberated at the various cathodes. For every 31.78 g. of copper deposited from the solution of cupric sulfate,

107.88 g. of silver was deposited from the solution of silver nitrate.

63.57 g. of copper was deposited from the solution of cuprous sulfate.

1.008 g. of hydrogen was evolved from the solution of sulfuric acid.

32.68 g. of zinc was deposited from the solution of zinc sulfate.

Inspection of these shows that they may be obtained in each case by dividing the atomic weight of the element by its valence. What does this mean? Simply that **the amounts of the various elements liberated by the same quantity of current are proportional to the atomic weights of the elements divided by their valence**, or, in other words, to their **combining weights**.

The quantity of electrical energy associated with one hydrogen ion is equal to that associated with one silver ion or with one NO_3 ion or one ion of any other monovalent element or radical. One ion of any divalent element or radical carries a quantity of electrical energy twice as great as that carried by a monovalent ion. A trivalent ion carries three times as much electrical energy as a

monovalent ion, etc. We can see from this why the weights of various elements liberated by the passage of the same quantity of current through the solution are in the proportion of the combining weights of these elements.

The unit of current, the ampere, is defined as that current which, under specified conditions, will liberate 0.001118 g. of silver in 1 sec. To liberate one gram weight of silver will require $107.88 \text{ sec.}/0.001118$ sec. for a current of 1 amp. or 48,247 sec. for a current of 1 amp., or, in general, 96,494 amp.-sec. (coulombs). This quantity of current, 96,494 amp.-sec., which will liberate one combi. g weight, or one gram-equivalent, of the substance at the electrodes is called a *Faraday*.

A *Faraday* will obviously liberate 1.008 g. of hydrogen. The quantity of hydrogen liberated by 1 amp. in 1 sec. is therefore $1.008 \text{ g.}/96,494 = 0.00001037 \text{ g.}$

From the known fact that 96,494 amp.-sec. will liberate one gram-equivalent of a substance we can calculate the weight of any given substance liberated in a definite time by a current of known strength.

POWER

The electric pressure applied between the electrodes drives the current through the solution: this electric pressure is called the voltage, or electromotive force (e.m.f.). The product of this force that tends to drive the current through the solution times the current that it drives gives the power required; *i.e.*,

$$P = EI$$

where E = the e.m.f. in volts.

I = the current in amperes.

P = the power in volt-amperes.

A volt-ampere is called a **watt**.

It is important to note that power represents the **rate** of doing work. If a train travels at the rate of 50 m.p.h. and keeps this up for 10 hr., the distance traveled will amount to the product of the rate of travel times the time. Similarly, if we multiply the rate at which electrical work is done by the length of time, we get the quantity of electrical work done. This quantity will naturally be expressed in the unit watts times

hours, or watt-hours, and this is the unit used in selling electrical energy.

The watt-hour is the amount of work done in one hour by an agent that does work at the rate of one watt; the kilowatt-hour is the amount of work done in one hour by an agent that does work at the rate of one kilowatt (1,000 watts).

RESISTANCE

The unit of electrical resistance is the **ohm**. This, like other units such as the meter and kilogram, is fixed in terms of a definite standard. The **ohm** is defined as the resistance offered to the passage of an electric current by a column of mercury 106.3 cm. in length and 1 sq. mm. in cross section at 0°C.

The resistance of, say, a wire is of course proportional to the length of the wire. If 1 ft. of a certain size and kind of wire has a resistance of a certain number of ohms, 2 ft. of this same wire will have a resistance equal to exactly twice this number of ohms. This resistance offered to the passage of current through any given material is dependent on the cross section. This is analogous to the flow of water through a pipe. The larger the cross section of the hole in the pipe the less resistance is offered to the flow of water. Someone has defined a wire, as far as flow of current through it is concerned, as being a hole in the air. The larger the hole the less resistance offered to the flow of current. As a matter of fact, the numerical effect of cross section is quantitative. The resistance is inversely proportional to the cross section.

The resistance in ohms of a cube of solution at 0°C. and 1 cm. on an edge is known as the **specific resistance**, or **resistivity**, of the solution. When this is known, and the dimensions of the electrodes and the distance between them are given, the resistance of the electrolyte between the electrodes can then be calculated.

Thus let L be the distance in centimeters between the electrodes, and S be the cross section or area of the electrodes (assume both electrodes to have the same area), and let K be the resistance of a cube of the solution, with edges 1 cm. long. The resistance of a chunk of the solution 1 sq. cm. in area and L cm. long will naturally be $L \times K$ ohms. The resistance of the total volume of

solution between the electrodes whose area is S sq. cm. will be LK/S , i.e.,

$$R = \frac{LK}{S}$$

where R = the resistance in ohms.

L = the distance between the electrodes in centimeters.

S = the area of each electrode. (Electrodes are usually assumed to be of equal area.)

K = the specific resistance of the solution in ohms.

The preceding formula simply means that the resistance of the solution is directly proportional to the length of the body of liquid between the electrodes and inversely proportional to its area.

The specific resistance of a few solutions is given below in ohms per centimeter cube at 18°C.

Solution	Strength, per cent	Gram equivalents per liter	Specific resistance
Cupric sulfate.....	10	1.387	31.25
Silver nitrate.....	5	0.307	39.06
Nickel sulfate.....	..	3.000	22.12
Sulfuric acid.....	5	1.053	4.80
Ammonium sulfate.....	5	0.778	18.11

The student is referred to Landolt-Börnstein-Roth-Scheel's *Physikalisch-chemische Tabellen* for extensive data on specific resistance.

Having calculated the resistance of the solution, we may then figure the voltage necessary to force a given current through the solution, by means of the relation:

$$E = RI$$

where E = the e.m.f. in volts.

R = the resistance in ohms.

I = the current in amperes.

This relation, which is an algebraic representation of Ohm's Law, simply shows that the current in amperes that flows

through, say, a solution is directly proportional to the electrical pressure in volts and inversely proportional to the resistance of the solution. Doubling the e.m.f. doubles the current that will flow through a given solution. Doubling the resistance, keeping the e.m.f. constant, will reduce the current to one-half.

Let us now consider a more practical problem which will serve to illustrate these relations.

Example.—What is the cost for power at 3¢ per kilowatt-hour to refine 1 lb. of copper in a cell containing a 10 per cent solution of copper sulfate at 18°C. and using electrodes of an area of 900 sq. cm., 10 cm. apart, the current strength being 5 amp.?

Since the resistance of the solution is proportional to the length of the column of the solution between the electrodes and inversely proportional to the area of this column, and since the specific resistance of the solution used is 31.25 ohms per centimeter cube, the resistance of the column of solution between the electrodes

$$R = \frac{31.25 \times 10}{900} = 0.3472 \text{ ohm}$$

Since the voltage necessary to force the current through the solution is proportional to the current strength and to the resistance, we have e.m.f. (voltage) = $5 \times 0.3472 = 1.7360$ volts. Now, we know that 1 amp. flowing for 1 sec. will liberate 0.00001037 g. of hydrogen; therefore 1 amp. flowing for 1 sec. will liberate

$$0.00001037 \times \frac{63.57}{2} = 0.0003292 \text{ g. of Cu}$$

One ampere flowing for 1 hr. will liberate

$$0.0003292 \times 3,600 = 1.185 \text{ g. of Cu}$$

Five amperes flowing for 1 hr. will liberate

$$5 \times 1.185 = 5.925 \text{ g. of Cu}$$

There is 453.6 g. in 1 lb.; hence to deposit 1 lb. of Cu will require 5 amp. of current for

$$\frac{453.6}{5.925} = 76.6 \text{ hr.}$$

Total quantity of current consumed will be

$$5 \times 76.6 = 383.0 \text{ amp.-hr.}$$

Since the power is equal to the voltage multiplied by the current, *i.e.*,

$$P = EI$$

power required = $5.0 \times 1.736 = 8.68$ watts.

8.68 watts used for 76.6 hr. = $8.68 \times 76.6 = 665$ watt-hr. = 0.665 kw.-hr. Cost of refining the copper per pound is, then,

$$0.665 \text{ kw.-hr.} \times 3 \text{ cts./kw.-hr.} = 2 \text{ cts.}$$

In commercial work, electric generators of 110 volts e.m.f. would be used. This voltage would force 5 amp. through $110/1.73 = 64$ cells like this one. Therefore, 64 of these cells would be connected together, and the current would flow from the cathode of one cell to the anode of the next, from the cathode of the second to the anode of the third, etc. This is spoken of as connecting the cells *in series*.

Problems

- 718.** Calculate the number of grams of copper that will be deposited in 5 hr. by a current of 5 amp. from a solution of CuSO_4 . *Ans.* 29.64 g.
- 719.** (a) How many coulombs of electricity will be necessary to deposit 2.5 g. of nickel from a solution of NiSO_4 ? (b) Calculate how many amperes will be necessary to deposit 2.5 g. of nickel in 10 min.
Ans. (a) 8,222 coulombs; (b) 13.70 amp.
- 720.** A 50-watt, 110-volt incandescent lamp is placed in series with an electrolytic cell containing a solution of zinc sulfate. Calculate the weight of the Zn that could be deposited in 1 hr. from the solution by the current that will flow. *Ans.* 0.5542 g.
- 721.** A current passed through a dilute hydrochloric acid solution for 20 min. liberated 100 cc. of hydrogen, at S.T.P. Calculate (a) the number of coulombs of electricity required, (b) the amperage needed.
Ans. (a) 861.5 coulombs; (b) 0.71 amp.
- 722.** A current is passed through a dilute sulfuric acid solution for 15 min. Fifty cubic centimeters of hydrogen at 22°C . and 750 mm. pressure is liberated. Calculate (a) the number of coulombs of electricity required, (b) the amperage needed.
Ans. (a) 396.6 coulombs; (b) 0.4407 amp.
- 723.** How much antimony will be deposited in 2 hr. by the passage of a current of 6 amp. through a solution of antimony trichloride?
Ans. 17.93 g.

724. A 100-watt, 110-volt incandescent lamp is placed in series with an electrolytic cell containing a dilute solution of phosphoric acid. Calculate the volume of hydrogen measured at 18°C . and 750 mm. pressure that will be liberated in 15 min. *Ans.* 102.6 cc.
725. It is desired to deposit 50 g. of tin from a stannous chloride solution with a current of 1 amp. How much time will be required? *Ans.* 22.58 hr.
726. A quantity of current passing through a solution of a cadmium salt deposited 1.02 g. of cadmium in 20 min. Calculate the amperage. *Ans.* 1.459 amp.
727. If a certain quantity of current deposits 20 g. of nickel, how many grams of platinum will be liberated by this same quantity of current from a solution of a platinic salt? *Ans.* 33.26 g.
728. A certain current can deposit 200 g. of zinc in 8 hr. What time will be required for this current to liberate a cubic meter of chlorine at 0°C . and 760 mm. pressure? *Ans.* 116.7 hr.
729. A current of 0.55 amp. was passed through a dilute sulfuric acid solution for 75 min. Calculate (a) the volume of hydrogen liberated at the cathode, (b) the volume of oxygen liberated at the anode. Both gases measured under standard conditions. *Ans.* (a) 287.2 cc.; (b) 143.6 cc.
730. A current of 0.1 amp. passing for 24 hr. through separate electrolytic cells containing solutions of HgCl_2 , $\text{Cd}(\text{NO}_3)_2$, and AgNO_3 , will deposit what respective weights of Hg, Cd, and Ag? *Ans.* 8.99 g. Hg; 5.02 g. Cd; 9.67 g. Ag.
731. How much silver will be deposited by a current of 1 amp. passing through a solution of silver nitrate in 1 sec.? How should you define an ampere on this basis?
732. How much copper will be deposited by a current of 0.5 amp. flowing for 30 min. through a solution of (a) cuprous chloride, (b) cupric chloride? *Ans.* (a) 0.5929 g.; (b) 0.2964 g.
733. Calculate the weight of Co deposited from a solution of a cobaltous salt by 247 coulombs. *Ans.* 7.10 g.
734. The specific resistance of a solution of nickel sulfate containing three gram-equivalents per liter is 22.12 ohms. The resistance of a certain volume of this solution between electrodes 20×20 cm. was found to be 1 ohm. Calculate the distance between the electrodes. *Ans.* 18.08 cm.
735. Calculate the cost for electrical energy necessary to produce 500 l. of hydrogen, at S.T.P., by electrolysis of a 5 per cent solution of sulfuric acid at 18°C . Electrodes 30×30 cm. Distance between electrodes 25 cm. Current 8 amp. Electrical energy costs 2¢ per kilowatt-hour. *Ans.* 2.55¢.
736. A copper-refining bath has 100 sets of electrodes (anode and cathode) connected in series. The electrolyte used is 10 per cent CuSO_4 solution at 18°C . Electrodes 100×100 cm., distance from anode to cathode is 7 cm. The e.m.f. between each pair, anode and cathode,

is 1 volt. Calculate (a) the power used, (b) the cost per pound of refining the copper, if the cost of electrical energy is 2¢ per kilowatt-hour.

Ans. (a) 4,571 watts; (b) 0.765¢.

- 737.** Calculate the cost per pound of refining nickel by electrolytic deposition, using a solution containing nickel sulfate and ammonium sulfate. The specific resistance of the solution is 15 ohms per centimeter cube. Distance between electrodes is 15 cm. Current density is 0.03 amp. per sq. cm. Electrical energy is available at 3¢ per kilowatt-hour.

Ans. 8.37¢.

- 738.** A 5 per cent silver nitrate solution is electrolyzed between silver electrodes 40×25 cm. and 10 cm. apart. Current density used is 0.025 amp. per sq. cm. Calculate (a) the voltage required, (b) the power required, (c) the length of time to deposit 20 kg. of silver.

Ans. (a) 9.765 volts; (b) 0.244 kw.; (c) 198.7 hr.

- 739.** A 5 per cent sulfuric acid solution is electrolyzed between electrodes 20×20 cm. and 20 cm. apart. Current density used is 0.05 amp. per sq. cm. Calculate (a) the voltage required, (b) the power, (c) the length of time to liberate 50 l. of hydrogen, at standard conditions.

Ans. (a) 4.8 volts; (b) 96 watts; (c) 5.98 hr.

- 740.** A 5 per cent solution of silver nitrate, a 5 per cent solution of sulfuric acid, and a 10 per cent solution of cupric sulfate are connected in series. All electrodes are 50×40 cm., and distance between anode and cathode is 20 cm. in each case. A current of 10 amp. is passed through all the solutions. Calculate (a) the voltage required, (b) the amounts of the three cations liberated in 5 hr.

Ans. (a) 7.511 volts; (b) 201.2 g. Ag, 1.86 g. H_2 , 59.28 g. Cu.

- 741.** The specific resistance of a silver-plating solution is 14.5 ohms per centimeter cube. Calculate the cost of electrical energy per ounce of silver deposited to silver-plate an object whose area is 478 sq. cm., using a current density of 0.04 amp. per sq. cm. Cost of electrical energy, 4¢ per kilowatt-hour. Average distance from anode to object, 12 cm.

Ans. 0.19¢.

- 742.** Calculate the cost of deposition of 25 g. of gold from a gold-plating solution containing gold in the auric condition the specific resistance of which is 12 ohms per centimeter cube. Area of electrodes, 200 sq. cm. Distance between electrodes, 20 cm. Current density, 0.05 amp. per sq. cm. Cost of electrical energy, 2¢ per kw.-hr.

Ans. 0.24¢.

CHAPTER XIV

OUTLINE

CHEMICAL EQUILIBRIUM. LECHATELIER'S PRINCIPLE.

REVERSIBLE REACTIONS.

An experiment with BiCl_3 shows that the reaction represented by the equation $\text{BiCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2\text{HCl}$ can go in either direction; *i.e.*, it is reversible.

The mechanism of a reversible reaction on the basis of ions.

THE LAW OF MASS ACTION (Guldberg and Waage).

The velocity of a reaction is proportional to the product of the concentrations of the reacting substances.

Derivation of an algebraic expression for the principle of mass action.

Concentrations must be in mols per unit volume.

COMMON ION EFFECT.

The ionization of acetic acid.

Derivation of the value of K , the ionization constant, of acetic acid.

The acidity of an acetic acid solution, *i.e.*, the hydrogen ion concentration, is reduced by the introduction of a soluble acetate into the solution.

Calculation of the extent to which the hydrogen ion concentration $[\text{H}^+]$ is reduced by the introduction of a soluble acetate.

Significance and determination of pH.

CHEMICAL EQUILIBRIUM; MASS ACTION; COMMON ION EFFECT

An equilibrium reaction is frequently referred to as a dynamic state, a condition in which two opposing tendencies ultimately balance one another. There are physical and chemical equilibriums. Any system in equilibrium is under the jurisdiction of the Principle of LeChatelier; *i.e.*, when a reaction in a state of equilibrium is subjected to a stress, such as changes in pressure, temperature, or concentration, the tendency is to shift the equilibrium in such a way as to relieve the stress, and a new equilibrium will be established under the new conditions. In

the manufacture of ammonia by the Haber process, we have an excellent application of the LeChatelier Principle. Briefly,



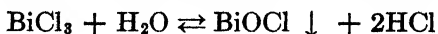
This equation tells us that

1 vol. of N_2 + 3 vols. of H_2 combine chemically to form 2 vols.
of NH_3

We note a shrinkage of 4 volumes of reactants to 2 volumes of the resultant. The application of pressure to this equilibrium system would tend to aid the formation of NH_3 , since an applied pressure would work in the same direction (to relieve the stress), *i.e.*, to a decrease in volume. The Claude process in the ammonia synthesis uses a pressure of 1,000 atmospheres for this reason. Since this equilibrium reaction is an exothermic reaction (heat is evolved), it is not advisable to operate this process at temperatures that are too high. This follows from the fact that an increase in temperature would favor the decomposition of ammonia into nitrogen and hydrogen, thus decreasing the percentage of ammonia. However, the speed of the reaction is considerably increased by the use of a catalyst. The equilibrium conditions for the industrial production of ammonia require a temperature of 450°C. to 600°C. , a pressure of 100 to 300 atmospheres, and a suitable catalyst.

Another example of chemical equilibrium is illustrated in the following example dealing with solutions.

If, to a concentrated solution of bismuth chloride in hydrochloric acid, water is slowly added, a white precipitate of BiOCl will form. Add hydrochloric acid a little at a time; when a certain amount has been added, the precipitate of BiOCl will dissolve. If more water is then added, the precipitate of BiOCl will form again. If, now, more HCl is again added, the precipitate again dissolves. These facts are represented by the equation

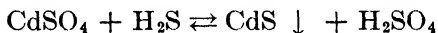


which is written with double arrows to indicate that the reaction can and does proceed in either direction. Under any specified set of conditions of concentration, temperature, and pressure, a condition of balance or equilibrium is reached. Corresponding

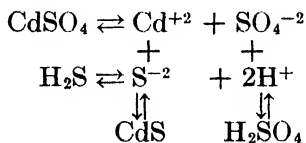
to this equilibrium there will be definite amounts of each of the four substances present. This state of equilibrium will not be one of rest, however, but the velocity of the reaction from left to right equals the velocity from right to left; *i.e.*, the number of molecules of BiOCl that are formed per second just equals the number of them that react with HCl per second to yield $\text{BiCl}_3 + \text{H}_2\text{O}$.

The foregoing experiment shows that when water is added, the reaction from left to right is favored, and more BiOCl is formed. It may also be stated that more of the other product, HCl , is formed. When HCl is added, the reaction from right to left is favored, BiOCl is seen to disappear, and BiCl_3 and H_2O are re-formed.

Such a reaction is said to be **reversible**. Many reactions met in the study of qualitative analysis are reversible. Consider the mechanism of such a reaction on the basis of ions. We shall use as an example the reaction of H_2S on CdSO_4 as indicated by the equation



CdSO_4 , H_2S , CdS , and H_2SO_4 ionize as indicated in the following scheme:



For any given number of cadmium ions and of sulfide ions in a given volume, there will be a certain number of collisions per second, and, corresponding to this, a certain number of molecules of CdS will be formed per second by the collisions of these oppositely charged ions.

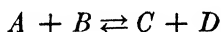
If the number of cadmium ions in the same volume of solution is, say, quadrupled, and the number of sulfide ions is kept the same, the number of collisions per second will be quadrupled, and the number of CdS molecules produced per second will be quadrupled. Similarly, if the number of cadmium ions is kept at the same original value, and the number of sulfide ions is quadrupled,

the number of molecules of CdS produced per second will be quadrupled. If the number of cadmium ions in the same volume of solution is quadrupled, and the number of sulfide ions is also quadrupled, the number of collisions per second and, consequently, the number of molecules of CdS produced per second will be 4×4 , or 16 times as great. In other words, the velocity of the reaction is proportional to the product of the numbers of the reacting molecules in any fixed volume; *i.e.*, **the velocity of the reaction is proportional to the product of the concentrations of the reacting ions.**

The principle thus indicated on the basis of reacting ions was derived from the results of exact experiments a great many of which were made by two Norwegian investigators, Guldberg and Waage. The principle is known as the Law of Mass Action and is applicable to homogeneous reversible reactions. For limitations the student should consult a text such as Stieglitz' "Qualitative Analysis."

DERIVATION OF ALGEBRAIC EXPRESSION FOR THE LAW OF MASS ACTION

Consider a reaction



In line with common practice $[A]$ **will be used to represent the concentration of the substance** A **in mols per liter.** Denote the velocity of the reaction from left to right by $v \rightarrow$; then

$$v \rightarrow \propto [A] \times [B], \text{ and therefore } v \rightarrow = K_1[A] \times [B]$$

where K_1 is a proportionality factor or number. Similarly,

$$v \leftarrow \propto [C] \times [D], \text{ and therefore } v \leftarrow = K_2[C] \times [D]$$

K_2 will be a different number from K_1 .

Now, in the beginning before any A and B have reacted, the concentrations of these are at the highest values; *i.e.*, $v \rightarrow$ is a maximum at the beginning of the reaction. On the other hand, no C or D is present at the start; therefore $v \leftarrow = 0$ at the start. As A and B react to produce C and D , the concentrations of A and B decrease, and consequently $v \rightarrow$ decreases. On the other hand, $v \leftarrow$ starts at zero and increases as the concentrations of C

and D become greater and greater. Finally, we reach a point of balance, or equilibrium, where the two velocities are equal; i.e., $v \rightarrow = v \leftarrow$. At this point

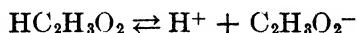
$$K_1[A] \times [B] = K_2[C] \times [D]$$

or, transposing,

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{K_1}{K_2} = K$$

K is, of course, simply a number or constant. It is the quotient of the two numbers K_1 and K_2 . K is called the *mass-action constant*, or equilibrium constant.

This general algebraic expression will be found very useful in studying reversible reactions, as we shall see. Consider as an example the ionization of a substance like acetic acid in aqueous solution. This ionization is a reversible reaction, as indicated by the equation



Since this is a reversible reaction, it is governed by the law of mass action. Without going through the algebraic process, we can at once decide that the following ionic relations will be true:

$$\frac{[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = K$$

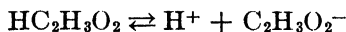
This expression states that the constant K is equal to the hydrogen ion concentration in mols per liter, $[\text{H}^+]$, times the acetate ion concentration in mols per liter, $[\text{C}_2\text{H}_3\text{O}_2^-]$, divided by the un-ionized acetic acid in mols per liter, $[\text{HC}_2\text{H}_3\text{O}_2]$.

The respective quantities of the three substances will always be such that the foregoing indicated quotient will always have a value numerically equal to K . The constant K which represents the relation between the concentrations of the ions and the un-ionized substance is called the **ionization constant**.

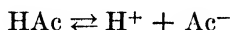
Instead of four substances— A , B , C , and D —we have only three, viz., H^+ , $\text{C}_2\text{H}_3\text{O}_2^-$, and $\text{HC}_2\text{H}_3\text{O}_2$. This does not alter the situation; it makes a simple relation with three factors instead of four.

Example 1.—A 0.1 *M* HC₂H₃O₂ solution is ionized to the extent of 1.3 per cent. Find the ionization constant of HC₂H₃O₂.

The ionization of HC₂H₃O₂ is expressed by



Frequently, for purposes of convenience, HC₂H₃O₂ is abbreviated to HAc where Ac = C₂H₃O₂. Then



The mass-action expression follows:

$$\frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = K_{(\text{ionisation})}$$

The value for [H⁺], *i.e.*, hydrogen ion concentration in mols per liter in a 0.1 *M* HAc solution, is

$$0.1 \text{ } M \times 0.013 = 0.0013 \text{ m./l.} = 1.3 \times 10^{-3} \text{ m./l.} = [\text{H}^+]$$

The [Ac⁻] is likewise = 0.0013 m./l. = 1.3×10^{-3} m./l.

The un-ionized HAc = [HAc] = 0.1 - 0.0013 = 0.0987 m./l. = 9.87×10^{-2} m./l.

Substituting in the mass-action formula,

$$\frac{(1.3 \times 10^{-3})(1.3 \times 10^{-3})}{(9.87 \times 10^{-2})} = 0.000018 = 1.8 \times 10^{-5} = K_{(\text{ionisation})}$$

A convention frequently employed in determining concentrations is to designate the gross concentration (molar) by *M* and the degree of ionization (as a decimal) by α . Then,

$$[\text{H}^+] = M\alpha; [\text{Ac}^-] = M\alpha; \text{ and } [\text{HAc}] = M(1 - \alpha).$$

The mass-action expression would be

$$\frac{(M\alpha)(M\alpha)}{M(1 - \alpha)} = \frac{M\alpha^2}{1 - \alpha} = \frac{0.1 \times (0.0013)^2}{1 - 0.0013} = 0.000018 = K_{(\text{ionisation})}$$

This formula has the advantage that if any two of the three quantities (concentration, degree of ionization, and ionization constant) are known, the third quantity is readily obtainable.

Example 2.—Find the degree of ionization of 0.2 *M* HAc. The ionization constant of HAc = 1.8×10^{-5} .

Applying the formula $\frac{M\alpha^2}{1-\alpha} = K_{(\text{ionisation})}$

$$\frac{0.2\alpha^2}{1-\alpha} = 1.8 \times 10^{-5}$$

$$0.2\alpha^2 = 1.8 \times 10^{-5} (1 - \alpha)$$

or

$$0.2\alpha^2 + 1.8 \times 10^{-5}\alpha - 1.8 \times 10^{-5} = 0$$

Solving this quadratic equation by the usual formula,

$$= \frac{-1.8 \times 10^{-5} + \sqrt{(1.8 \times 10^{-5})^2 + 4 \times 0.2(1.8 \times 10^{-5})}}{2 \times 0.2}$$

$$= 0.0038, \text{ or } 0.38 \text{ per cent}$$

Example 3.—Determine the concentration at which acetic acid is 0.2 per cent ionized.

$$\frac{M\alpha^2}{1-\alpha} = K$$

$$\frac{M(0.002)^2}{1-0.002} = 1.8 \times 10^{-5}$$

$$M = \frac{(1.8 \times 10^{-5})(0.998)}{0.4 \times 10^{-5}} = 4.5 \text{ } M$$

It is essential to grasp the idea that the value of $K_{(\text{ionisation})}$ will not change, even though the concentration of the solution is changed or some other acetate is present in the same solution. The following table illustrates the constancy of K despite changes

Concentration of solution, mols per liter	Per cent ionization	K
0.1	1.34	.00182
0.08	1.50	.000183
0.03	2.45	.000185
0.01	4.17	.00181

in the concentration of the solution. It gives the experimentally determined value of the percentage ionization of acetic acid and

the value of K for solutions of acetic acid of different concentrations. It will be noted that for a tenfold change in the concentration of the solution the value of K remains constant within the limit of error of such measurements.

Example 4.—Consider, now, the effect produced by dissolving 0.1 gram-mol of ammonium acetate (7.7 g.) in 1 l. of 0.1 M HAc. The NH_4Ac ionizes as follows:



It is to be noted that salts are, in general, quite highly ionized, even though the acid from which they are derived is weakly ionized. When the NH_4Ac is added to the original HAc solution, the acetate ion concentration increases tremendously. These Ac^- ions, in turn, tend to tie up H^+ ions; and as a consequence the ionization of acetic acid is repressed, resulting in a decrease in the acidity of the solution. This can also be ascertained from the mass-action expression. If the ionization constant is to be maintained at a definite value, K , and if the $[\text{Ac}^-]$ is increased, then in the ratio $[\text{H}^+][\text{Ac}^-]/[\text{HAc}]$ the $[\text{H}^+]$ must decrease, since $[\text{HAc}]$ cannot increase to any great extent because of low ionization.

Now, the $K_{(\text{ionization})}$ for HAc = 1.8×10^{-5} , and the problem is to determine the $[\text{H}^+]$ in a solution that is 0.1 M in HAc and 0.1 M in NH_4Ac . Assume that the NH_4Ac is 80 per cent ionized.

The $[\text{Ac}^-]$ from NH_4Ac = 0.1 0.8 = 0.08 m./l.

Let $x = [\text{H}^+]$ and $[\text{Ac}^-]$ from HAc; then $(0.1 - x)$ m./l. = $[\text{HAc}]$

The total $[\text{Ac}^-]$ in the solution = $(0.08 + x)$ m./l.

Substituting in the mass-action expression,

$$\frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{(0.08 + x)}{(0.1 - x)} = 1.8 \times 10^{-5}$$

Since x is small, we can avoid the solving of a quadratic equation obtained above by neglecting x with regard to 0.1 and 0.08. Thus,

$$\begin{aligned} \frac{0.08x}{0.1} &= 1.8 \times 10^{-5} \\ x &= 2.2 \times 10^{-5} \text{ m./l.} = [\text{H}^+] \end{aligned}$$

That is to say, the $[H^+]$ has been decreased from 0.0013 m./l., or 1.3×10^{-3} m./l., to 2.2×10^{-5} m./l., or $0.000022/0.0013 = \frac{1}{60}$ of its former value.

The decrease in the $[H^+]$ or decrease in the ionization of HAc brought about by the high concentration of the Ac^- furnished by NH_4Ac is known as the **common ion effect**. In general terms, the common ion effect can be defined as follows: If to a solution of a weak electrolyte (a slightly ionized substance) one adds a strong electrolyte which has an ion in common with the weak one, the ionization of the weak electrolyte is greatly repressed.

It is to be kept in mind that the concentration values used in the mass-action expression must be in the terms of mols per unit volume—not in grams per unit volume. The velocity of the reaction is proportional to the **number of molecules** or **ions** that react and not to the gross weight in grams. In cases where the quantities used are expressed in grams or in cubic centimeters of a solution of definite strength, etc., it is necessary first to transform these quantities to *mols per unit volume*. This is illustrated in the following examples:

Example 5.—Calculate the magnesium ion concentration in mols per liter $[Mg^{+2}]$ in a solution containing 0.2 g. of $MgCl_2$ in 100 cc. of solution. Assume complete ionization of the magnesium chloride.

The solution contains 0.2 g. of $MgCl_2$ per 100 cc. of solution, or 2 g./l. of $MgCl_2$.

1 gram-mol of $MgCl_2$ contains 95.22 g. of $MgCl_2$.

Then 95.22 g./l. of $MgCl_2$ represents a concentration of 1 m./l. of $MgCl_2$.

2 g./l. of $MgCl_2$ represents a concentration of $\frac{2}{95.22}$, or 0.021 mol per liter of $MgCl_2$, or 0.021 M . $M =$ molarity.

Since the $MgCl_2$ is assumed to be 100 per cent ionized, then 0.021 m./l. $= [Mg^{+2}]$.

Example 6.—Find the molarity of a hydrochloric acid solution that contains 2.5 cc. of 6 N HCl in 100 cc. of solution.

Solution.—Since 2.5 cc. of 6 N HCl is diluted to 100 cc., the concentration of the hydrochloric acid is reduced in the inverse proportion to the increase of volume, so that the normality now becomes $2.5/100 \times 6 N$, or 0.15 N .

A normal solution of HCl is the same as a molar solution of HCl.

Then the foregoing solution is 0.15 *M* with respect to HCl.

SIGNIFICANCE AND DETERMINATION OF pH

Pure water is ionized to a very small extent according to the ionic equation



Applying the Law of Mass Action, we obtain

$$\frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]} = K$$

On account of its slight dissociation, any change in $[\text{H}^+]$ or $[\text{OH}^-]$ will have only a slight effect on the value for $[\text{H}_2\text{O}]$. In fact, $[\text{H}_2\text{O}]$ may be considered as a constant. If we designate the value $[\text{H}_2\text{O}]$ as K_1 , then

$$\frac{[\text{H}^+] \times [\text{OH}^-]}{K_1} = K \text{ or } [\text{H}^+] \times [\text{OH}^-] = K_1 \times K = K_{\text{H}_2\text{O}}$$

$K_{\text{H}_2\text{O}}$ equals the ion product for water. By experiment the numerical value for $K_{\text{H}_2\text{O}} = 1 \times 10^{-14}$ at 25°C. Thus, the product of the concentration of H^+ and OH^- has a constant value $= 1 \times 10^{-14}$. If $[\text{H}^+]$ is made small, then $[\text{OH}^-]$ will be correspondingly larger, and vice versa.

In pure water, the value for $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}$ m./l. Since water is a neutral substance, it is possible to define a neutral solution as one that has a value for $[\text{H}^+]$ or $[\text{OH}^-] = 1 \times 10^{-7}$ m./l.

Suppose that we have a slightly acid solution, the $[\text{H}^+]$ of which has been determined to be 1×10^{-6} m./l. Applying the equation

$$\begin{aligned} [\text{H}^+] \times [\text{OH}^-] &= 1 \times 10^{-14} \\ [\text{OH}^-] &= \frac{1 \times 10^{-14}}{1 \times 10^{-6}} = 1 \times 10^{-8} \text{ m./l.} \end{aligned}$$

It follows that a solution in which $[\text{H}^+] > 10^{-7}$ or the $[\text{OH}^-] < 10^{-7}$ is an acid solution or gives an acid reaction. Also, a solution in which $[\text{H}^+] < 10^{-7}$ or the $[\text{OH}^-] > 10^{-7}$ is an alkaline solution or gives a basic reaction.

It is customary, now, to use the system of expressing the acidity or alkalinity of a solution in terms of the logarithm of reciprocal of the $[H^+]$, and this is known as the "pH" value. Then

$$pH = \log \frac{1}{[H^+]}$$

Suppose that $[H^+]$ of a solution is 1×10^{-3} m./l., then

$$pH = \log \frac{1}{10^{-3}} = \log 10^3 = 3$$

The following table shows the relationship between the $[H^+]$ and the pH values.

	Acid								Neu- tral	Alkaline							
$[H^+]$	$10^{-0.5}$	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}		10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}	
pH	0.5	1	2	3	4	5	6		7	8	9	10	11	12	13	14	

Thus, an acid solution is one in which $[H^+] > 10^{-7}$, or $pH < 7$.

A neutral solution is one in which $[H^+] = 10^{-7}$, or $pH = 7$.

An alkaline solution is one in which $[H^+] < 10^{-7}$, or $pH > 7$.

Consideration will now be given to examples illustrating typical calculations.

Example 1.—Calculate the pH value for a solution in which the $[H^+] = 3 \times 10^{-3}$ m./l.

$$\begin{aligned} pH &= \log \frac{1}{[H^+]} = \log \frac{1}{3 \times 10^{-3}} = \log \frac{10^3}{3} \\ &= \log 10^3 - \log 3 = 3.0 - 0.48 = 2.52 \end{aligned}$$

since $pH = 2.52$, $[H^+] = 10^{-2.52}$ and $[OH^-] = 10^{-11.48}$.

Example 2.—Calculate the $[H^+]$ of a solution that has a pH value of 6.5.

$$pH = \log \frac{1}{[H^+]} = 6.5$$

$$\frac{1}{[H^+]} = \text{antilogarithm } 6.5 = 10^6 \times 3.1$$

$$[H^+] = \frac{1}{3.1 \times 10^6} = 0.30 \times 10^{-6} = 3.0 \times 10^{-7} \text{ m./l.}$$

Check:

$$\text{pH} = \log \frac{1}{[\text{H}^+]} = \log \frac{1}{3.0 \times 10^{-7}} = \log \frac{10^7}{3} = 7 - 0.47 = 6.5$$

Problems

- 743.** What is the molar concentration of a cadmium sulfate solution that contains 250 mg. of CdSO_4 per 100 cc. of solution? *Ans.* 0.0119 *M*.
- 744.** If 0.75 g. of lead chloride is dissolved in 1 l. of solution, what is its molar concentration? *Ans.* 0.00269 *M*.
- 745.** A solution is known to contain 8 cc. of 6 *N* $\text{HC}_2\text{H}_3\text{O}_2$ and 16 cc. of 6 *N* $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in 400 cc. of solution. Determine the molar concentration of each of these substances in this solution.
Ans. 0.12 *M* $\text{HC}_2\text{H}_3\text{O}_2$; 0.24 *M* $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.
- 746.** A solution contains 2 cc. of 5 *N* NH_4OH and 10 cc. of 5 *N* NH_4Cl in 50 cc. of solution. Calculate the molar concentration of each of these substances in this solution. *Ans.* 0.2 *M* NH_4OH ; 1 *M* NH_4Cl .
- 747.** If 5 cc. of hydrochloric acid (sp. gr. 1.1983 and containing 39.86 per cent by weight of HCl) is diluted to 50 cc., what is the $[\text{H}^+]$ of the solution if the hydrochloric acid is assumed to be 78 per cent ionized?
Ans. 1.002 m./l.
- 748.** Calculate the $[\text{H}^+]$ of a solution of sulfuric acid that contains 8 cc. of 36 *N* H_2SO_4 in 100 cc. of solution. The sulfuric acid is assumed to be 45 per cent ionized. *Ans.* 0.648 m./l.
- 749.** Calculate the number of grams of lead chloride present in a solution that contains the equivalent of 3.36×10^{-4} m./l. of Pb^{+2} .
Ans. 0.0934 g.
- 750.** A solution contains 0.0048 g. of CdCl_2 in 100 cc. Calculate the $[\text{Cd}^{+2}]$ of this solution, assuming complete dissociation of the CdCl_2 .
Ans. 2.6×10^{-4} m./l.
- 751.** A solution contains 0.027 g. of PbCl_2 in 100 cc. Assume complete dissociation of the PbCl_2 . Calculate the $[\text{Pb}^{+2}]$ of this solution.
Ans. 9.7×10^{-4} m./l.
- 752.** Calculate the molar concentration of a solution of potassium chromate that contains 0.5 cc. of 2 *N* K_2CrO_4 in 100 cc. *Ans.* 0.05 *M*.
- 753.** Calculate the ionization constant for 0.1 *M* solution of (a) ammonium hydroxide that is 0.4 per cent ionized, (b) hydrofluoric acid that is 7.0 per cent ionized. *Ans.* (a) 1.6×10^{-6} ; (b) 5.25×10^{-4} .
- 754.** Calculate the ionization constant for a 0.1 *M* solution of hydrocyanic acid that is 0.01 per cent ionized. *Ans.* 1×10^{-9} .
- 755.** Calculate the H^+ ion concentration in a 0.5 *M* $\text{HC}_2\text{H}_3\text{O}_2$ solution. The ionization constant for acetic acid is 1.8×10^{-5} .
Ans. 2.99×10^{-3} m./l.
- 756.** Calculate the OH^- ion concentration in a 0.05 *M* NH_4OH solution. The ionization constant for ammonium hydroxide is 1.8×10^{-5} .
Ans. 9.39×10^{-4} m./l.

757. Calculate the H^+ ion concentration in a 0.2 *M* HCN solution. The ionization constant for hydrocyanic acid is 7.0×10^{-10} .
Ans. 1.179×10^{-5} m./l.
758. Calculate the degree of ionization for a 0.38 *N* NH_4OH solution. The ionization constant for ammonium hydroxide is 9.55×10^{-6} .
Ans. 0.499 per cent.
759. The ionization constant for a 0.1 *M* HNO_2 solution is 5×10^{-4} . Calculate the degree of ionization.
Ans. 6.82 per cent.
760. Calculate the degree of ionization for a 0.05 *M* $HC_2H_3O_2$ solution. The ionization constant for acetic acid is 1.8×10^{-5} . *Ans.* 1.87 per cent.
761. The ionization constant for acetic acid is 1.8×10^{-5} . Calculate the degree of ionization of 0.04 *M* $HC_2H_3O_2$ solution. *Ans.* 2.09 per cent.
762. Calculate the pH for each of the following solutions in which the $[H^+]$ values are, respectively, (a) 5×10^{-6} , (b) 7.3×10^{-7} .
Ans. (a) 5.3; (b) 6.14.
763. Calculate the pH values corresponding to each of the following $[H^+]$ values: (a) 2.6×10^{-5} , (b) 5.9×10^{-10} . *Ans.* (a) 4.6; (b) 9.2.
764. Calculate the $[H^+]$ and $[OH^-]$ in (a) 0.2 *N* HCl that is 90 per cent ionized, (b) 0.05 *N* HCl that is 93 per cent ionized. Express the $[H^+]$ obtained in (a) and (b) as pH.
Ans. (a) $[H^+] = 0.12 = 10^{-0.92}$, $[OH^-] = 8.3 \times 10^{-14} = 10^{-13.08}$,
 pH = 0.92
 (b) $[H^+] = 0.047 = 10^{-1.33}$, $[OH^-] = 2.15 \times 10^{-13}$,
 pH = 1.33 = $10^{-12.67}$.
765. Calculate the $[H^+]$ corresponding to the following pH values:
 (a) 6.2, (b) 2.3. *Ans.* (a) 6×10^{-7} ; (b) 5×10^{-3} .
766. Change the following pH values to $[H^+]$: (a) 5.6, (b) 9.5.
Ans. (a) 2.5×10^{-6} ; (b) 3×10^{-10} .
767. Calculate the $[H^+]$ corresponding to each of the following pH values:
 (a) 7.6, (b) 4.05. *Ans.* (a) 2.5×10^{-8} ; (b) 1×10^{-5} .
768. Calculate the pH and $[OH^-]$ in (a) 0.01 *N* HCl solution that is 92 per cent ionized, (b) 0.001 *N* NaOH solution assuming complete ionization.
Ans. (a) pH = 2.04; $[OH^-] = 0.91 \times 10^{-12} = 10^{-11.96}$.
 (b) pH = 11; $[OH^-] = 10^{-3}$.
769. Calculate the pH of (a) 0.1 *N* $HC_2H_3O_2$ solution that is 1.34 per cent ionized; (b) 0.1 *N* NH_4OH solution that is ionized to the extent of 1.2 per cent.
Ans. (a) pH = 2.87; (b) pH = 11.11.
770. Calculate the pH of (a) 0.05 *M* HCN that is ionized to the extent of 0.01 per cent, (b) 0.01 *M* $HC_2H_3O_2$ that is 4.15 per cent ionized.
Ans. (a) pH = 5.30; (b) pH = 3.38.
771. Calculate the pH and $[OH^-]$ of (a) 0.08 *M* $HC_2H_3O_2$ that is 1.50 per cent ionized, (b) 0.001 *M* HCl that is 100 per cent ionized.
Ans. (a) pH = 2.92; $[OH^-] = 1.5 \times 10^{-12} = 10^{-11.18}$.
 (b) pH = 3; $[OH^-] = 10^{-11}$.
772. Calculate the $[H^+]$ in a solution that is 0.5 *M* in $HC_2H_3O_2$ and *M* in $NH_4C_2H_3O_2$. The ammonium acetate is assumed to be 80 per cent ionized. The $K_{(ionisation)}$ of acetic acid is 1.8×10^{-5} .
Ans. 1.1×10^{-5} m./l.

- 773.** Calculate the $[\text{OH}^-]$ in a solution that is 0.5 *N* in NH_4OH and 2*M* in NH_4Cl . The ammonium chloride is assumed to be 80 per cent ionized. The $K_{(\text{ionization})}$ of ammonium hydroxide is 1.8×10^{-5} .
Ans. 5.6×10^{-6} m./l.
- 774.** A solution is 2 *N* in NH_4OH (0.3 per cent ionized). Find (a) the $K_{(\text{ionization})}$ of ammonium hydroxide, and (b) determine the concentration at which NH_4OH is 1 per cent ionized.
Ans. (a) 1.8×10^{-5} ; (b) 0.179 m./l.
- 775.** Calculate the $[\text{H}^+]$ in a solution that contains 7.7 g. of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ and 8 cc. of 6 *N* $\text{HC}_2\text{H}_3\text{O}_2$ in a volume of 400 cc. Assume complete ionization of ammonium acetate. The acetic acid is assumed to be 1.5 per cent ionized. The $K_{(\text{ionization})}$ for acetic acid is 1.8×10^{-5} .
Ans. 1.95×10^{-5} m./l.
- 776.** Determine the $[\text{H}^+]$ in 100 cc. of acetic acid solution that is 0.1 *M* in $\text{HC}_2\text{H}_3\text{O}_2$ and to which sufficient $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ has been added to increase the $[\text{C}_2\text{H}_3\text{O}_2^-]$ to 0.200 m./l. The $K_{(\text{ionization})}$ for acetic acid is 1.8×10^{-5} , and the acetic acid is 1.3 per cent ionized.
Ans. 9×10^{-4} m./l.

Additional Problems without Answers, for Quizzes

- 777.** The ionization constant for HCN is 7×10^{-10} . The degree of ionization of hydrocyanic acid is 0.01 per cent. Calculate (a) the molar concentration of the acid, (b) the H^+ ion concentration.
- 778.** The ionization constant for NH_4OH is 1.8×10^{-5} . The ammonium hydroxide is ionized to the extent of 0.5 per cent. Determine (a) the molar concentration of the base, (b) the OH^- ion concentration.
- 779.** Calculate the H^+ ion concentration in a 0.1 *M* HCN solution. The ionization constant for hydrocyanic acid is 7×10^{-10} .
- 780.** Calculate the H^+ ion concentration in a 0.5 *M* $\text{HC}_2\text{H}_3\text{O}_2$ solution. The ionization constant for acetic acid is 1.8×10^{-5} .
- 781.** Calculate the OH^- ion concentration in a 0.2 *M* NH_4OH solution. The ionization constant is 1.8×10^{-5} .
- 782.** Calculate the $[\text{OH}^-]$ in 100 cc. of ammonium hydroxide solution that is 0.2 *M* in NH_4OH and to which sufficient NH_4Cl has been added to increase the $[\text{NH}_4^+]$ to a value of 0.500 m./l. The ammonium hydroxide is 1.2 per cent ionized. The $K_{(\text{ionization})}$ for NH_4OH is 1.8×10^{-5} .
- 783.** The $K_{(\text{ionization})}$ for NH_4OH is 1.8×10^{-5} . Determine the $[\text{OH}^-]$ in an ammonium hydroxide solution that is 0.5 *M* in NH_4OH . If this solution is made 2.5 *M* in NH_4Cl , what is the new $[\text{OH}^-]$? Assume the ammonium chloride to be 80 per cent ionized.
- 784.** Determine the acetate ion concentration required to reduce the $[\text{H}^+]$ in a solution that is 0.1 *M* in $\text{HC}_2\text{H}_3\text{O}_2$ to 4.5×10^{-6} m./l.
- 785.** Find the $[\text{NH}_4^+]$ necessary to reduce to a value of 1×10^{-6} m./l. the $[\text{OH}^-]$ in a solution that is 0.2 *M* in NH_4OH .
- 786.** Calculate the $[\text{H}^+]$ in 1 l. of solution that is 0.1 *M* in $\text{HC}_2\text{H}_3\text{O}_2$ and 0.1 *M* in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. The $K_{(\text{ionization})}$ for acetic acid is 1.8×10^{-5} . The ammonium acetate is 80 per cent ionized.

- 787.** Calculate the $[\text{OH}^-]$ in a liter of solution that is 0.1 *M* in NH_4OH and 0.5 *M* in NH_4Cl . The ammonium chloride is 80 per cent ionized. The $K_{(\text{ionization})}$ for NH_4OH is 1.8×10^{-5} .
- 788.** The $K_{(\text{ionization})}$ for acetic acid is 1.8×10^{-5} . Determine the concentration at which $\text{HC}_2\text{H}_3\text{O}_2$ will be 0.6 per cent ionized.
- 789.** At what concentration will NH_4OH be 0.8 per cent ionized? The $K_{(\text{ionization})}$ for NH_4OH is 1.8×10^{-5} .

CHAPTER XV

OUTLINE

Saturated solutions and supersaturated solutions from the point of view of kinetics.

Solubility. The solubilities of slightly soluble substances are most conveniently expressed in terms of the ions that they furnish in solution.

Solubility product constant. Solubility of slightly soluble substances expressed as the product of the concentrations of the ions furnished by the dissolved substance.

Calculations of the S.P.C. for $[\text{Ba}^{+2}] \times [\text{CO}_3^{-2}]$ from the solubility of BaCO_3 in grams per liter.

The separation of the cations of Groups 2 and 3 in qualitative analysis, by H_2S .

$$[\text{H}^+]^2 \times [\text{S}^{-2}] = 1.1 \times 10^{-23} = K_{(\text{ionization})}$$

The concentration of sulfide ion, $[\text{S}^{-2}]$, is regulated by addition of a definite amount of HCl to the solution. This HCl ionizes and furnishes a definite concentration of hydrogen ions, $[\text{H}^+]$.

By suitable adjustment of the $[\text{H}^+]$, the $[\text{S}^{-2}]$ is made to assume a value high enough to precipitate second-group cations rather completely as sulfides but not high enough to precipitate third-group cations at the same time; *i.e.* $[\text{S}^{-2}] \times (\text{second-group cation}) > \text{solubility product of these metallic sulfides}$; but $[\text{S}^{-2}] \times (\text{third-group cation}) < \text{solubility product of these metallic sulfides}$.

The high value of $[\text{S}^{-2}]$ in alkaline solution such as used for the precipitation of Group 3 causes complete precipitation of Group 3 cations as sulfides.

Hydrolysis.

SOLUBILITY. SOLUBILITY PRODUCT

When a soluble solid substance is placed in water, molecules of the substance leave the solid and dissolve in the water, thus producing a solution. As the molecules of substance accumulate in the solution, some of them, in their rapid motion, return again to the solid and become attached to it. As the number of dissolved molecules increases, the number that returns to the solid in any given length of time increases. This process continues until finally the crowding is so great that the number

of molecules that dissolve from the solid per unit of time is just equal to the number that returns to the solid per unit of time from the crowded solution. There is no further change in the quantity, but the action is proceeding in both directions continuously. When this condition of physical equilibrium ($A_{\text{solid}} \rightleftharpoons A_{\text{dissolved}}$) is reached, we say that the solution is **saturated** with this substance at this temperature. Other substances may be dissolved in this same solution until the rate at which the molecules of the second substance dissolve equals the rate at which molecules deposit from the solution on the solid.

If the temperature of the solution is raised, the speed of the molecules is increased, and in nearly all cases the solubility of the substance is increased.

If we take a solution that is *saturated* with a given substance, filter it, and then cool the saturated solution, molecules of the dissolved substance would have a tendency to leave the solution in the solid form, thus diminishing the number of them per unit volume of solution in accord with the general effect of temperature on solubility. The exchange process would continue until the number of molecules that leaves the solution per second, under the new condition, equals the number that dissolves per second. But no solid is present. It was filtered off.

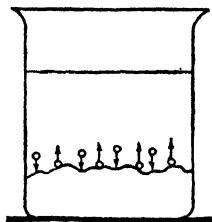


FIG. 17.

Solutions, not further disturbed, have the property of remaining in this abnormal overcrowded condition *i.e.*, unstable state. If a crystal of the substance is introduced, immediate precipitation of the substance from the overcrowded solution will be observed. A solution in this condition is said to be **supersaturated**.

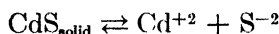
The solubility of substances in water varies widely; some are very soluble, some only slightly so, and many are said to be insoluble in water. However, there is no such thing as complete insolubility; and when we say that a substance is insoluble, we really mean that its solubility is extremely small.

The solubility of a slightly soluble substance is conveniently expressed in terms of the concentration of the ions (mols per liter) that it furnishes in a saturated solution of that substance. From previous discussion, the equilibrium conditions existing in a

saturated solution of a slightly soluble substance like cadmium sulfide can be expressed as follows:



It is to be noted that the cadmium sulfide in dilute solution undergoes practically complete ionization, so that equilibrium should be represented by



The Cd^{+2} concentration in mols per liter = $[\text{Cd}^{+2}]$

The S^{-2} concentration in mols per liter = $[\text{S}^{-2}]$

The $\text{CdS}_{\text{solid}}$ concentration in mols per liter = $[\text{CdS}]$

Substituting these concentrations in the mass-action expression, we obtain

$$\frac{[\text{Cd}^{+2}][\text{S}^{-2}]}{[\text{CdS}_{\text{solid}}]} = K$$

Now, the $[\text{CdS}_{\text{solid}}]$ represents the concentration of a solid compound that is a constant = k' ; then

$$[\text{Cd}^{+2}][\text{S}^{-2}] = k'K = K \text{ (Solubility product constant, abbreviated S.P.C.)}$$

Thus the *product of the ion concentrations* (mols per liter) in a saturated solution of a slightly soluble substance is called the **solubility product constant**, or simply **S.P.C.**

Emphasis should be placed on the fact that ion concentrations are expressed in mols per liter (m./l.).

Some textbooks use the term "gram-ions per liter" to express concentrations of ions. For the sake of uniformity, the procedure adopted in this text is to use the general term "mols per liter"—for expressing concentrations of both molecules and ions.

Example 1.—The solubility of BaCO_3 at 24.2°C . is 0.0024 g. per 100 cc. Determine the S.P.C. for BaCO_3 .

$$0.0024 \text{ g. per 100 cc.} = 0.024 \text{ g./l.}$$

1 gram-mol of BaCO_3 contains 197.37 g. of BaCO_3 .

197.37 g./l. of BaCO_3 represents a concentration of 1 m./l. of BaCO_3 .

0.024 g./l. of BaCO_3 represents a concentration of $0.024/197.37 \text{ m./l.} = 1.2 \times 10^{-4} \text{ m./l.}$

Since BaCO_3 is a strong electrolyte, we shall consider that it is completely ionized in this dilute solution into Ba^{+2} and CO_3^{-2} . Then

$$[\text{Ba}^{+2}] = 1.2 \times 10^{-4} \text{ m./l.}, \text{ and } [\text{CO}_3^{-2}] = 1.2 \times 10^{-4} \text{ m./l.}$$

and

$$[\text{Ba}^{+2}] \times [\text{CO}_3^{-2}] = (1.2 \times 10^{-4}) \times (1.2 \times 10^{-4}) = 1.44 \times 10^{-8} \\ = \text{S.P.C.}$$

This value for the S.P.C. of BaCO_3 has the following significance: This S.P.C. might be called a saturation value for BaCO_3 , since it is obtained from its solubility at a given temperature, which in turn represents an equilibrium condition or state of saturation of this slightly soluble substance. Then, if the circumstances are such that the product of the ion concentrations exceeds 1.44×10^{-8} , precipitation of BaCO_3 will take place. On the other hand, should the ion concentration product be less than 1.44×10^{-8} , no precipitation will occur, or a condition of unsaturation exists.

The Solubility Product Principle is of considerable aid in qualitative chemical analysis, particularly in dealing with controlled and selective precipitation. One is able to determine the minimum quantity of precipitant required to bring about precipitation of a given ion of known concentration, or just what values must be maintained to prevent precipitation of certain groups of ions and permit the separation of other ion groups. Further extension of the Solubility Product Principle follows.

Example 2.—The solubility of silver chromate, Ag_2CrO_4 , is $3.6 \times 10^{-3} \text{ g. per 100 cc.}$ Assuming that the Ag_2CrO_4 is 90 per cent ionized, determine its S.P.C.

$$3.6 \times 10^{-3} \text{ g. per 100 cc.} = 3.6 \times 10^{-2} \text{ g./l.}$$

1 gram-mol of Ag_2CrO_4 contains 331.77 g. of Ag_2CrO_4 .

$3.6 \times 10^{-2} \text{ g./l.}$ of Ag_2CrO_4 represents a concentration of $3.6 \times 10^{-2}/331.77 \text{ m./l.} = 0.000108 \text{ m./l.} = 1.08 \times 10^{-4} \text{ m./l.}$
= molarity of Ag_2CrO_4 .



Since the Ag_2CrO_4 is assumed to be 90 per cent ionized, $(1.08 \times 10^{-4}) \times 0.90 = 0.000097$, or 9.7×10^{-5} m./l. = concentration of each ion furnished by Ag_2CrO_4 .

From the foregoing ionic equation, it is noted that 1 mol of Ag_2CrO_4 yields 2 mols of Ag^+ and 1 mol of CrO_4^{-2} ; then in the foregoing saturated solution of Ag_2CrO_4 ,

1.08×10^{-4} m./l. of Ag_2CrO_4 yields $2 \times (9.7 \times 10^{-5})$ m./l. of Ag^+ and 9.7×10^{-5} m./l. of CrO_4^{-2} .

The total Ag^+ concentration = $[\text{Ag}^+] = 2 \times (9.7 \times 10^{-5})$ m./l. = 1.94×10^{-4} m./l.

The total CrO_4^{-2} concentration = $[\text{CrO}_4^{-2}] = 9.7 \times 10^{-5}$ m./l.

The S.P.C. of $\text{Ag}_2\text{CrO}_4 = [\text{Ag}^+]^2 \times [\text{CrO}_4^{-2}] = (1.94 \times 10^{-4})^2 \times (9.7 \times 10^{-5}) = 3.6 \times 10^{-12}$

It is important at this stage to emphasize the fact that in the S.P.C. expression the *concentrations are total ion concentrations* and the *coefficient of the ions*, as shown by the ionic equation, *appears as exponents* in the S.P.C. formula. Thus, in the foregoing example, there are two Ag^+ furnished by the ionization of Ag_2CrO_4 ; the concentration of each $\text{Ag}^+ = 9.7 \times 10^{-5}$ m./l.; and since there are 2Ag^+ , the total silver ion concentration, represented by $[\text{Ag}^+]$, is $2 \times 9.7 \times 10^{-5}$ m./l. This is the value that is squared or raised to the power of 2 in the S.P.C. expression. Since there is only one CrO_4^{-2} , the total chromate ion concentration, or $[\text{CrO}_4^{-2}]$, = 9.7×10^{-5} m./l.

Example 3.—The S.P.C. for Ag_2CrO_4 is 3.6×10^{-12} . Determine the minimum $[\text{CrO}_4^{-2}]$ required to bring about precipitation of Ag_2CrO_4 from a solution known to contain 5 cc. of 0.5 M AgNO_3 in 100 cc. Assume the AgNO_3 to be completely ionized.

The molarity of 5 cc. of 0.5 M AgNO_3 in 100 cc. is $\frac{5}{100} \times 0.5 M = 0.025 M$ AgNO_3 .

Since AgNO_3 is 100 per cent ionized, 0.025 m./l. = $[\text{Ag}^+]$

$$[\text{Ag}^+]^2 \times [\text{CrO}_4^{-2}] = (0.025)^2 \times [\text{CrO}_4^{-2}] = 3.6 \times 10^{-12}$$

$$[\text{CrO}_4^{-2}] = \frac{3.6 \times 10^{-12}}{(2.5 \times 10^{-2})^2} = 5.76 \times 10^{-9} \text{ m./l.}$$

This is the quantity of CrO_4^{-2} that will just start precipitation of Ag_2CrO_4 in the foregoing AgNO_3 solution.

Example 4.—The S.P.C. of $\text{PbF}_2 = 3.2 \times 10^{-8}$. Calculate the $[\text{Pb}^{+2}]$ in a saturated solution of lead fluoride.

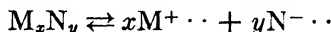
The S.P.C. of $\text{PbF}_2 = [\text{Pb}^{+2}] \times [\text{F}^-]^2 = 3.2 \times 10^{-8}$

Let $x = [\text{Pb}^{+2}]$.

Then

$$\begin{aligned} 2x &= [\text{F}^-] \\ [\text{Pb}^{+2}] \times [\text{F}^-]^2 &= x \times (2x)^2 = 3.2 \times 10^{-8} = 32.0 \times 10^{-9} \\ 4x^3 &= 32.0 \times 10^{-9} \\ x^3 &= 8.0 \times 10^{-9} \\ x &= 2.0 \times 10^{-3} \text{ m./l.} = [\text{Pb}^{+2}] \end{aligned}$$

To reiterate: if M_xN_y represents 1 mol of a slightly soluble substance, the ionization of which can be represented by



$[\text{M}^{+ \cdot \cdot}]$ represents the **total ion concentration** of $\text{M}^{+ \cdot \cdot}$ in mols per liter and **involves** the coefficient x .

$[\text{N}^{- \cdot \cdot}]$ represents the **total ion concentration** of $\text{N}^{- \cdot \cdot}$ in mols per liter and **involves** the coefficient y .

The S.P.C. expression becomes

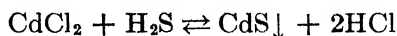
$$[\text{M}^{+ \cdot \cdot}]^x \times [\text{N}^{- \cdot \cdot}]^y = K = \text{S.P.C. of } \text{M}_x\text{N}_y$$

PRECIPITATION WITH HYDROGEN SULFIDE IN QUALITATIVE CHEMICAL ANALYSIS

Separation of Group 2 from Group 3. Effect of H^+ Ion Concentration.—In qualitative analysis the separation of Group II cations (Hg^{+2} , Pb^{+2} , Bi^{+3} , Cu^{+2} , Cd^{+2} , As^{+3} , Sb^{+3} , Sn^{+4}) in a hydrochloric acid medium with hydrogen sulfide from those of Group III (Al^{+3} , Cr^{+3} , Zn^{+2} , Fe^{+3} , Mn^{+2} , Co^{+2} , Ni^{+2}) affords an excellent example of selective precipitation. The division into these groups is, however, not so sharply defined as indicated. If an excessive quantity of HCl is present in a solution containing the cations of both groups, the sulfides of Cd^{+2} , Pb^{+2} , and Sn^{+4} are incompletely precipitated by H_2S , and considerable amounts of these cations escape precipitation. On the other hand, if the HCl present in the solution when Group II is precipitated by H_2S is less than a certain definite amount, the sulfides of Zn^{+2} , Co^{+2} , and Ni^{+2} are partially precipitated with Group II.

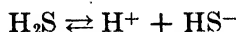
It is a fact that a great many of the sulfides of Group II cations are quite soluble in solutions of high hydrochloric acid

concentration. Consider a representative sulfide precipitation such as CdS from CdCl_2 solution:



This is a reversible reaction and as such is governed by the Mass Action Law. If the CdCl_2 solution contains a high concentration of HCl to begin with, it is obvious that when this solution is saturated with H_2S a condition prevails in which no CdS will be precipitated; *i.e.*, the S.P.C. for CdS will not be exceeded. In order to precipitate CdS, the S^{-2} concentration must be so regulated that, for a given Cd^{+2} concentration, the S.P.C. for CdS will be exceeded. Let us see how this can be accomplished.

Hydrogen sulfide is only slightly soluble in water, and a saturated solution of it is frequently called hydrosulfuric acid. It is a very weak dibasic acid, and its small ionization proceeds in two steps. The first, or primary, ionization is small and shown by



The secondary ionization of the hydrosulfide ion, HS^- , is much smaller than the primary ionization:



The mass-action expression for the total ionization of H_2S is

$$\frac{[\text{H}^+]^2 \times [\text{S}^{-2}]}{[\text{H}_2\text{S}]} = K_{\text{ionization}}$$

The total ionization of H_2S in a saturated solution gives values of $[\text{H}^+] = 0.95 \times 10^{-4}$ m./l. and $[\text{S}^{-2}] = 1.2 \times 10^{-15}$ m./l. The value for $[\text{H}_2\text{S}]$ is practically a constant. Then

$$[\text{H}^+]^2 \times [\text{S}^{-2}] = K = 1.1 \times 10^{-23}$$

This constant for a saturated solution of H_2S for all intents and purposes can be considered as a S.P.C. for H_2S and enables one to control the sulfide ion concentration by regulating the H^+ concentration. In reality, this controlling of the S^{-2} concentration is an example of the common ion effect. H_2S is a weak electrolyte, and the addition of HCl, a strong electrolyte, to a saturated solution of H_2S will repress the ionization of the H_2S .

In other words, the large increase in H^+ concentration will cause a decrease in the S^{-2} concentration in order to maintain constancy of the ion product for H_2S .

Example 1.—Find the S^{-2} concentration in a solution of 0.3 M HCl that has been saturated with H_2S . Assume the HCl to be 90 per cent ionized.

$$0.3 M \times 0.9 = 0.27 \text{ m./l.} = [H^+] \text{ from } HCl$$

Neglecting the small amount of $[H^+]$ from H_2S ,

$$[H^+]^2 \times [S^{-2}] = 1.1 \times 10^{-23}$$

$$(0.27)^2 [S^{-2}] = 1.1 \times 10^{-23}$$

$$[S^{-2}] = 1.5 \times 10^{-22} \text{ m./l.}$$

Example.—(a) The S.P.C. of PbS is 3.4×10^{-28} . If a solution contains 0.001 m./l. of Pb^{+2} , what S^{-2} concentration will be required to precipitate PbS ? (b) If the foregoing solution is saturated with H_2S , what value of $[H^+]$ would have to be maintained to prevent precipitation of PbS ? The S.P.C. for H_2S is 1.1×10^{-23} .

$$(a) [Pb^{+2}][S^{-2}] = 3.4 \times 10^{-28} = \text{S.P.C.}_{PbS}.$$

$$[Pb^{+2}] = 0.001 \text{ m./l.}$$

Substituting in the formula for S.P.C._{PbS},

$$(0.001)[S^{-2}] = 3.4 \times 10^{-28}$$

$$[S^{-2}] = 3.4 \times 10^{-25} \text{ m./l.}$$

$$(b) [H^+]^2 \times [S^{-2}] = 1.1 \times 10^{-23} = \text{S.P.C.}_{H_2S}$$

Substituting in the formula for S.P.C._{H₂S},

$$[H^+]^2(3.4 \times 10^{-25}) = 1.1 \times 10^{-23}$$

$$[H^+]^2 = 35.35$$

$$[H^+] = 5.7 \text{ m./l.}$$

Any value of $[H^+]$ greater than 5.7 m./l. would prevent precipitation of PbS . (Why?)

Example 3.—A solution is 0.1 M in Cd^{+2} and 0.3 M in HCl . This solution is saturated with H_2S . The S.P.C. for CdS is 3.6×10^{-29} . The HCl is assumed to be 90 per cent ionized. How much Cd^{+2} escapes precipitation as CdS ?

$$0.3 M \times 0.9 = 0.27 \text{ m./l.} = [\text{H}^+]$$

$$[\text{H}^+]^2[\text{S}^{-2}] = 1.1 \times 10^{-23} = \text{S.P.C.}_{\text{H}_2\text{S}}$$

$$(0.27)^2[\text{S}^{-2}] = 1.1 \times 10^{-23}$$

$$[\text{S}^{-2}] = 1.5 \times 10^{-22} \text{ m./l.}$$

$$[\text{Cd}^{+2}][\text{S}^{-2}] = 3.6 \times 10^{-29}$$

$$[\text{Cd}^{+2}](1.5 \times 10^{-22}) = 3.6 \times 10^{-29}$$

$$[\text{Cd}^{+2}] = 2.4 \times 10^{-7} \text{ m./l. escapes precipitation.}$$

Example 4.—An acid solution that is 0.01 *M* in Pb^{+2} and Mn^{+2} is saturated with H_2S . What is the range of $[\text{H}^+]$ for selective precipitation of PbS in the presence of Mn^{+2} ?

$$\text{S.P.C. for PbS} = 3.4 \times 10^{-28}$$

and

$$\text{S.P.C. for MnS} = 1.4 \times 10^{-15}$$

$$(a) \quad [\text{Pb}^{+2}][\text{S}^{-2}] = 3.4 \times 10^{-28}$$

$$(0.01)[\text{S}^{-2}] = 3.4 \times 10^{-28}$$

$[\text{S}^{-2}] = 3.4 \times 10^{-26} \text{ m./l.} = \text{concentration of } \text{S}^{-2} \text{ at which precipitation of PbS will begin.}$

$$[\text{H}^+]^2[\text{S}^{-2}] = 1.1 \times 10^{-23}$$

$$[\text{H}^+]^2(3.4 \times 10^{-26}) = 1.1 \times 10^{-23}$$

$$[\text{H}^+]^2 = 323$$

$$[\text{H}^+] = 18 \text{ m./l.}$$

$$(b) \quad [\text{Mn}^{+2}][\text{S}^{-2}] = 1.4 \times 10^{-15}$$

$$(0.01)[\text{S}^{-2}] = 1.4 \times 10^{-15}$$

$[\text{S}^{-2}] = 1.4 \times 10^{-13} \text{ m./l.} = \text{concentration of } \text{S}^{-2} \text{ at which precipitation of MnS will begin.}$

$$[\text{H}^+]^2[\text{S}^{-2}] = 1.1 \times 10^{-23}$$

$$[\text{H}^+]^2(1.4 \times 10^{-13}) = 1.1 \times 10^{-23}$$

$$[\text{H}^+]^2 = 0.78 \times 10^{-10}$$

$$[\text{H}^+] = 8.8 \times 10^{-6} \text{ m./l.}$$

The $[\text{H}^+]$ range from 18 m./l. to $8.8 \times 10^{-6} \text{ m./l.}$ permits the precipitation of PbS in the presence of Mn^{+2} .

The precipitation of metallic sulfides with ammonium sulfide, $(\text{NH}_4)_2\text{S}$, affords another application of the solubility product principle. The usual procedure is to make the solution containing the cations basic with NH_4OH and then pass H_2S into the solution

which forms $(\text{NH}_4)_2\text{S}$. The ionization of $(\text{NH}_4)_2\text{S}$ is very much greater than that of a saturated solution of H_2S and as a consequence a higher concentration of S^{-2} prevails, which causes precipitation of various sulfides. In fact, those sulfides which are incompletely precipitated in an acid medium are readily precipitated in the basic solution.

Example.—Suppose that a solution of ammonium sulfide is 0.1 *M* in $(\text{NH}_4)_2\text{S}$ and that it ionizes to the extent of 50 per cent. What quantity of Pb^{+2} and Zn^{+2} remain unprecipitated in 100 cc. of solution? The S.P.C. for $\text{PbS} = 3.4 \times 10^{-28}$, and S.P.C. for $\text{ZnS} = 1.2 \times 10^{-23}$.

$$0.1 \text{ } M \times 0.5 = 0.05 \text{ m./l.} = [\text{S}^{-2}] \text{ from } 0.1 \text{ } M (\text{NH}_4)_2\text{S}$$

Substituting in the S.P.C. formulas,

$$\begin{aligned} [\text{Pb}^{+2}][\text{S}^{-2}] &= [\text{Pb}^{+2}](0.05) = 3.4 \times 10^{-28} \\ [\text{Pb}^{+2}] &= 6.8 \times 10^{-27} \text{ m./l.,} \end{aligned}$$

or 6.8×10^{-28} m./100 cc. of Pb^{+2} escapes precipitation

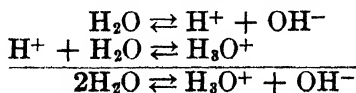
$$\begin{aligned} [\text{Zn}^{+2}][\text{S}^{-2}] &= [\text{Zn}^{+2}](0.05) = 1.2 \times 10^{-23} \\ [\text{Zn}^{+2}] &= 2.4 \times 10^{-22} \text{ m./l.,} \end{aligned}$$

or 2.4×10^{-23} m./100 cc. of Zn^{+2} escapes precipitation.

It should be noted that these values or $[\text{Pb}^{+2}]$ and $[\text{Zn}^{+2}]$ are extremely small and that therefore practically complete precipitation of PbS and ZnS in the solution takes place when $(\text{NH}_4)_2\text{S}$ is the precipitant.

HYDROLYSIS

In Chaps. IX and XIV attention was called to the slight ionization of pure water. That is, pure water shows a small electrical conductivity. The ionization of water is represented by



The ionization constant for water (slightly ionized) is obtained from the following mass-action expression:

$$\frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} = K_{\text{ionization}}$$

In water

$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

Since $[\text{H}_2\text{O}]$ is a constant of k' , we may write

$$[\text{H}_3\text{O}^+][\text{OH}^-] = k' \times K = K_{(\text{ion product for water})}, \text{ or } K_{(\text{H}_2\text{O})}$$

At equilibrium,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ m./l.}$$

Then

$$(1 \times 10^{-7}) \times (1 \times 10^{-7}) = 1 \times 10^{-14} = K_{(\text{H}_2\text{O})}$$

The product of the concentrations of H_3O^+ and OH^- is a constant. If $[\text{H}_3\text{O}^+]$ is made small, $[\text{OH}^-]$ will become large in order to maintain the constancy of $K_{(\text{H}_2\text{O})}$.

Many aqueous salt solutions give either an acid or a basic reaction with litmus. This results from the reaction of water with the salt to form an acid and a base. It is, in fact, the opposite of neutralization and is called hydrolysis.

Hydrolysis, or hydrolytic action, is prominent with salts of a strong base and a weak acid or salts of a weak base and a strong acid. It does not take place when salts of a strong base and a strong acid react with water. In the case of salts of a weak acid and a weak base, there is considerable hydrolytic action.

The mechanism of hydrolysis may be considered from the following viewpoint. Suppose the salt sodium acetate, NaAc , is dissolved in water. It is a salt of a strong base, NaOH , and a weak acid, HAc . It is also a strong electrolyte, thereby yielding a high concentration of Na^+ and Ac^- in dilute solution. Now, the ionization of water is represented by

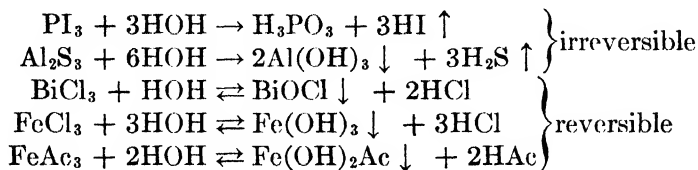


The acetate ions Ac^- from NaAc unite with the hydronium ion (H_3O^+) to form the slightly ionized HAc . This results in a decrease in the H_3O^+ concentration and an increase in the OH^- concentration, since the $K_{\text{H}_2\text{O}}$ is always constant and equal to 1×10^{-14} . The $[\text{OH}^-]$ being larger than $[\text{H}_3\text{O}^+]$, gives rise to a basic reaction with litmus.

An aqueous solution of NH_4Ac is considerably hydrolyzed, even though it is a salt of a weak acid and a weak base, yet its

solution is neutral. This is accounted for by the fact that NH_4OH and HAc are weak electrolytes, with $K_{\text{ionisation}}$ for each at about the same value.

Certain hydrolytic actions involve the formation of volatile compounds and also insoluble compounds. These are exemplified by the following reactions:



To be sure, the mass-action principle applies to hydrolysis (reversible) reactions, and one is able to determine the hydrolysis constant $K_{(\text{hydrolysis})}$ and the degree of hydrolysis of salt reactions.

Example 1.—Determine the $[\text{OH}^-]$ and the $[\text{HAc}]$ as a result, of the hydrolysis of a 0.01 M NaAc solution, assuming complete ionization of NaAc .

The following two equilibriums exist in the foregoing hydrolysis:

$$\frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = K_{(\text{ionisation})} = 1.8 \times 10^{-5}$$

and

$$[\text{H}^+][\text{OH}^-] = K_{(\text{H}_2\text{O})} = 1 \times 10^{-14}$$

Dividing one expression by the other,

$$\frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]} = \frac{K_{(\text{H}_2\text{O})}}{K_{(\text{ionisation})}} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10} = K_{(\text{hydrolysis of NaAc})} \quad (1)$$

Let $x = [\text{OH}^-] = [\text{HAc}]$.

Then

$$(0.01 - x) = [\text{Ac}^-]$$

Substituting these values in (1)

$$\frac{x \times x}{(0.01 - x)} = 5.5 \times 10^{-10}$$

At equilibrium $[\text{Ac}^-]$ is practically equal to 0.01, the concentration of NaAc. The x in the denominator may be disregarded, and the expression simplifies to

$$\frac{x^2}{0.01} = 5.5 \times 10^{-10}$$

$$x = 2.3 \times 10^{-6} \text{ m./l.} = [\text{OH}^-] = [\text{HAc}]$$

Example 2.—Calculate (a) the hydrolysis constant for NH_4Cl and (b) the $[\text{OH}^-]$ in 0.1 *M* NH_4Cl solution.

Equilibrium is acquired in this solution when the $K_{\text{ionisation}}$ of NH_4OH and $K_{\text{H}_2\text{O}}$ are satisfied.

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = 1.75 \times 10^{-5}, \text{ and } [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

Dividing one expression by the other

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{NH}_4^+][\text{OH}^-]/[\text{NH}_4\text{OH}]} = \frac{K_{\text{H}_2\text{O}}}{K_{(\text{ionisation})}}$$

or

$$\frac{[\text{H}^+][\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = \frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10} = K_{(\text{hydrolysis})} \quad (\text{II})$$

As in Example 1, we let $x = [\text{H}^+] = [\text{NH}_4\text{OH}]$ and $(0.1 - x) = [\text{NH}_4^+]$. Substituting in (II),

$$\frac{x \times x}{(0.1 - x)} = 5.7 \times 10^{-10}$$

Neglecting the x in the denominator, owing to the fact that $[\text{NH}_4^+]$ is practically equal to the original concentration of NH_4Cl , or 0.1, then

$$\frac{x^2}{0.1} = 5.7 \times 10^{-10}$$

$$x = 7.5 \times 10^{-6} = [\text{H}^+]$$

Since

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} = K_{(\text{H}_2\text{O})}$$

$$[\text{H}^+] = 7.5 \times 10^{-6} \text{ m./l.}$$

Substituting,

$$(7.5 \times 10^{-6})[\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{OH}^-] = 1.3 \times 10^{-9}$$

It is apropos to state that even in strongly basic solutions the $[H^+]$ does not reach zero; *i.e.*, there are H^+ ions in a strongly basic solution, and likewise there are OH^- ions in a strongly acid solution. To illustrate this, the following examples are presented.

Example 1.---Determine the $[OH^-]$ in a 0.1 *M* HCl solution that is 90 per cent ionized.

$$\begin{aligned}0.1 \times 0.9 &= 0.09 \text{ m./l.} = [H^+] \text{ from HCl} \\[H^+][OH^-] &= 1 \times 10^{-14} = K_{(H_2O)} \\[H^+] &= 0.09 \text{ m./l.}\end{aligned}$$

Substituting,

$$\begin{aligned}(0.09)[OH^-] &= 1 \times 10^{-14} \\[OH^-] &= 1.1 \times 10^{-13} \text{ m./l.}\end{aligned}$$

Example 2.---The $K_{\text{ionization}}$ for HAc is 1.8×10^{-5} . Calculate the $[OH^-]$ in a 0.01 *N* HAc solution.

$$\begin{aligned}\frac{M\alpha^2}{(1-\alpha)} &= 1.8 \times 10^{-5} = K_{\text{ionization}} \\ \alpha &= \text{degree of ionization} \\ \frac{0.01\alpha^2}{1-\alpha} &= 1.8 \times 10^{-5}\end{aligned}$$

Since HAc is a weak electrolyte, the denominator of the foregoing expression $(1 - \alpha)$ will approach unity, and

$$\begin{aligned}0.01\alpha^2 &= 1.8 \times 10^{-5} \\ \alpha &= 4 \times 10^{-2} = 0.04 = \text{degree of ionization}\end{aligned}$$

Now,

$$\begin{aligned}0.01M \times 0.04 &= 0.0004 \text{ m./l.} = 4 \times 10^{-4} \text{ m./l.} = [H^+] \\[H^+][OH^-] &= 1 \times 10^{-14} = K_{(H_2O)} \\[H^+] &= 4 \times 10^{-4} \text{ m./l.}\end{aligned}$$

Substituting,

$$\begin{aligned}(4 \times 10^{-4})[OH^-] &= 1 \times 10^{-14} \\[OH^-] &= 2.5 \times 10^{-11} \text{ m./l.}\end{aligned}$$

Problems

- 790.** The solubility of $MgCO_3$ in water is 4.3×10^{-1} g./l. Calculate the solubility product $[Mg^{+2}] \times [CO_3^{-2}]$. **Ans.** 2.59×10^{-5} .

- 791.** The solubility of AgI in water is 3.0×10^{-6} g./l. Calculate the solubility product $[\text{Ag}^+] \times [\text{I}^-]$. *Ans.* 1.61×10^{-16} .
- 792.** The solubility of BaSO_4 is 2.5×10^{-3} g./l. Calculate the solubility product $[\text{Ba}^{+2}] \times [\text{SO}_4^{-2}]$. *Ans.* 1.14×10^{-10} .
- 793.** The solubility of BaCrO_4 is 3.8×10^{-3} g./l. Calculate the solubility product $[\text{Ba}^{+2}] \times [\text{CrO}_4^{-2}]$. *Ans.* 2.22×10^{-10} .
- 794.** The solubility of Ag_3PO_4 is 6.5×10^{-3} g./l. Calculate the solubility product $[\text{Ag}^+]^3 \times [\text{PO}_4^{-3}]$. *Ans.* 1.55×10^{-18} .
- 795.** The solubility of MgNH_4PO_4 is 8.6×10^{-3} g./l. Calculate the solubility product $[\text{Mg}^{+2}] \times [\text{NH}_4^+] \times [\text{PO}_4^{-3}]$. *Ans.* 2.44×10^{-13} .
- 796.** The solubility of CaSO_4 is 2.00 g./l. Calculate the solubility product $[\text{Ca}^{+2}] \times [\text{SO}_4^{-2}]$. Assume the ionization of the CaSO_4 to be 95 per cent. *Ans.* 1.94×10^{-4} .
- 797.** The solubility product $[\text{Pb}^{+2}] \times [\text{SO}_4^{-2}]$ is 1.92×10^{-8} . Calculate the solubility of PbSO_4 in grams per liter. *Ans.* 4.18×10^{-2} g./l.
- 798.** The solubility product $[\text{Ca}^{+2}] \times [\text{C}_2\text{O}_4^{-2}]$ is 3.9×10^{-9} . Calculate the solubility of CaC_2O_4 in grams per liter. *Ans.* 7.94×10^{-3} g./l.
- 799.** The solubility product $[\text{Ca}^{+2}] \times [\text{SO}_4^{-2}]$ is 1.94×10^{-4} . Assuming the salt to be 95 per cent ionized, calculate the solubility of CaSO_4 in grams per liter. *Ans.* 1.99 g./l.
- 800.** The S.P.C. for silver bromide is 0.77×10^{-12} . Determine its solubility in water in (a) grams per liter; (b) gram-mols per liter. *Ans.* (a) 1.6×10^{-4} g./l.
- 801.** The S.P.C. for lead chromate is 1.77×10^{-14} . Determine its solubility in water in (a) grams per liter; (b) gram-mols per liter. *Ans.* (a) 4.3×10^{-6} g./l.
- 802.** Find the solubility of lead iodide in (a) grams per liter; (b) gram-mols per liter. The S.P.C. for PbI_2 is 1.39×10^{-8} . *Ans.* (a) 7.0×10^{-1} g./l.
- 803.** Find the range of $[\text{SO}_4^{-2}]$ for the selective precipitation of SrSO_4 in the presence of Ca^{+2} . The concentration of the cations is 0.3 *M*. The S.P.C. for SrSO_4 is 3×10^{-7} , and the S.P.C. for CaSO_4 is 6×10^{-5} . *Ans.* 1×10^{-6} m./l. to 2×10^{-4} m./l.
- 804.** Find the range of $[\text{S}^{-2}]$ for the selective precipitation of (a) CuS in the presence of Pb^{+2} ; (b) HgS in the presence of Pb^{+2} . The concentration of the cations is 0.2 *M*.
S.P.C. for CuS is 1.8×10^{-42} ; S.P.C. for HgS is 3.0×10^{-54} .
S.P.C. for PbS is 3.4×10^{-28} .
Ans. (a) 9×10^{-42} m./l. to 1.7×10^{-27} m./l.
(b) 1.5×10^{-53} m./l. to 1.7×10^{-27} m./l.
- 805.** Calculate the weight of MnCl_2 that escapes precipitation in a solution, containing the cations of Group 3, that is 0.01 *M* with respect to $(\text{NH}_4)_2\text{S}$. Assume the ammonium sulfide to be 55 per cent ionized. The S.P.C. for MnS = 1.4×10^{-15} . *Ans.* 3.20×10^{-11} g./l.
- 806.** Calculate the weight of ZnCl_2 that escapes precipitation in a solution, containing the cations of Group 3, that is 0.2 *M* with respect to $(\text{NH}_4)_2\text{S}$. Assume the ammonium sulfide to be 55 per cent ionized. The S.P.C. for ZnS = 1.2×10^{-23} . *Ans.* 1.49×10^{-20} g./l.

807. Calculate the weight of FeCl_2 that escapes precipitation in a solution, containing the cations of Group 3, that is 0.1 M with respect to $(\text{NH}_4)_2\text{S}$. Assume the ammonium sulfide to be 55 per cent ionized. The S.P.C. for $\text{FeS} = 1.5 \times 10^{-19}$. *Ans.* 3.45×10^{-16} g./l.
808. By calculations, show that the quantity of CdCl_2 that escapes precipitation is negligible in a solution containing the cations of Groups 2 and 3, which is 0.25 M with respect to $(\text{NH}_4)_2\text{S}$. Assume the ionization of ammonium sulfide to be 55 per cent. The S.P.C. of $\text{CdS} = 3.6 \times 10^{-29}$. *Ans.* 4.80×10^{-26} g./l.

Additional Problems without Answers, for Quizzes

809. The solubility of silver arsenite in 100 g. of water at 20°C . is 1.15×10^{-3} g. Calculate the solubility product $[\text{Ag}^+]^3 \times [\text{AsO}_3^{-3}]$.
810. The solubility of silver arsenate in 100 g. of water at 20°C . is 8.5×10^{-4} g. Calculate the solubility product $[\text{Ag}^+]^3 \times [\text{AsO}_4^{-3}]$.
811. The solubility of silver sulfide in 100 g. of water at 20°C . is 1.4×10^{-5} g. Calculate the solubility product $[\text{Ag}^+]^2 \times [\text{S}^{-2}]$.
812. The solubility of silver acetate in 100 g. of water at 0°C . is 0.72 g., and at 80°C . it is 2.52 g. Calculate the solubility product $[\text{Ag}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]$ at these two different temperatures.
813. The solubility of mercuric iodide at 25°C . is 5.91×10^{-3} g. Calculate the solubility product $[\text{Hg}^{+2}] \times [\text{I}^-]^2$.
814. The solubility of AgCl is 1.5×10^{-4} g. per 100 cc.; the solubility of Ag_2CrO_4 is 2.5×10^{-3} g. per 100 cc. Assuming complete ionization of each salt, calculate the $[\text{Ag}^+]$ furnished in a saturated solution of each salt.
815. The solubility of AgBr is 8.4×10^{-6} g. per 100 cc.; the solubility of Ag_2SO_4 is 8×10^{-1} g. per 100 cc. Assuming complete ionization of each salt, calculate the $[\text{Ag}^+]$ furnished in a saturated solution of each silver salt.
816. The solubility of AgI is 3.0×10^{-7} g. per 100 cc.; the solubility of Ag_3PO_4 is 6.5×10^{-4} g. per 100 cc. Assuming complete ionization in the saturated solution of each salt, calculate the $[\text{Ag}^+]$ in each solution.
817. The S.P.C. of $\text{AgCl} = 1.2 \times 10^{-10}$; the S.P.C. of $\text{Ag}_2\text{C}_2\text{O}_4 = 6.2 \times 10^{-12}$. By calculations show which of these two silver salts furnishes the smaller $[\text{Ag}^+]$.
818. The S.P.C. of $\text{PbCrO}_4 = 1.8 \times 10^{-14}$; the S.P.C. of $\text{PbI}_2 = 1.4 \times 10^{-8}$. Calculate the $[\text{Pb}^{+2}]$ in each of these saturated lead salt solutions.
819. The S.P.C. of $\text{Ag}_2\text{S} = 1.6 \times 10^{-49}$; the S.P.C. of $\text{PbS} = 3.4 \times 10^{-28}$. Calculate the minimum $[\text{S}^{-2}]$ required to start precipitation of each of these sulfides.
820. The S.P.C. of $\text{BaSO}_4 = 1.2 \times 10^{-10}$; the S.P.C. of $\text{PbSO}_4 = 1.92 \times 10^{-8}$. Calculate the minimum $[\text{SO}_4^{-2}]$ required to start precipitation of each of these two sulfates.
821. A solution contains 200 mg. of ferric chloride in 100 cc. Assume the ionization of the ferric chloride in this solution to be 60 per cent. The

- solubility product $[\text{Fe}^{+3}] \times [\text{OH}^{-}]^3 = 1.1 \times 10^{-36}$. Calculate the minimum amount of $[\text{OH}^{-}]$ necessary to start precipitation of $\text{Fe}(\text{OH})_3$.
- 822.** A solution contains 200 mg. of aluminum chloride in 100 cc. Assume the ionization of the aluminum chloride in this solution to be 60 per cent. The solubility product $[\text{Al}^{+3}] \times [\text{OH}^{-}]^3 = 1.1 \times 10^{-15}$. Calculate the minimum amount of $[\text{OH}^{-}]$ necessary to start precipitation of $\text{Al}(\text{OH})_3$.
- 823.** Determine the $[\text{Pb}^{+2}]$ in a solution that is 0.3 *M* in HCl (90 per cent ionized) and saturated with H_2S .
S.P.C. for H_2S is 1.1×10^{-23} ; S.P.C. for PbS is 3.4×10^{-28} .
- 824.** Calculate the $[\text{H}^{+}]$ that will prevent the precipitation of NiS by H_2S in a solution that is 0.1 *M* in Ni^{+2} .
S.P.C. for H_2S is 1.1×10^{-23} ; S.P.C. for NiS is 1.0×10^{-27} .
- 825.** Calculate the $[\text{Cd}^{+2}]$ in a solution that is 0.3 *M* in H^{+} and is saturated with H_2S .
S.P.C. for H_2S is 1.1×10^{-23} ; S.P.C. for CdS is 3.6×10^{-29} .
- 826.** Determine the $[\text{H}^{+}]$ that will prevent the precipitation of MnS by H_2S in a solution that is 0.1 *M* in Mn^{+2} .
S.P.C. for H_2S is 1.1×10^{-23} ; S.P.C. for MnS is 1.4×10^{-15} .
- 827.** Determine the $[\text{H}^{+}]$ that will prevent the precipitation of ZnS by H_2S in a solution that is 0.2 *M* in Zn^{+2} .
S.P.C. for H_2S is 1.1×10^{-23} ; S.P.C. for ZnS is 1.2×10^{-23} .
- 828.** Find the range of $[\text{H}^{+}]$ that will be required for the selective precipitation of (a) PbS in the presence of Ni^{+2} ; (b) CdS in the presence of Fe^{+2} . The cation concentrations are 0.1 *M*.
S.P.C. for H_2S is 1.1×10^{-23} ; S.P.C. for PbS is 3.4×10^{-28} ;
S.P.C. for NiS is 1.0×10^{-27} ; S.P.C. for FeS is 1.5×10^{-19} .
- 829.** The S.P.C. for $\text{Mg}(\text{OH})_2$ is 3.6×10^{-11} . What is the minimum $[\text{OH}^{-}]$ required to start precipitation of $\text{Mg}(\text{OH})_2$ in a solution that is 0.1 *M* in Mg^{+2} ?
- 830.** A solution is considered to be 0.01 *M* in $(\text{NH}_4)_2\text{S}$ (assumed to be 55 per cent ionized). Show by calculations that practically complete precipitation of Pb^{+2} , Zn^{+2} , and Mn^{+2} in 100 cc. of this solution takes place.
S.P.C. for PbS is 3.4×10^{-28} ; S.P.C. for ZnS is 1.2×10^{-23} ;
S.P.C. for MnS is 1.4×10^{-15} .
- 831.** Find the range of $[\text{CrO}_4^{-2}]$ for the selective precipitation of BaCrO_4 in the presence of Sr^{+2} . The concentration of the cations is 0.2 *M*. The solubility of BaCrO_4 is 1.48×10^{-5} m./l., and the solubility of SrCrO_4 is 5.9 m./l. Assume the ionization of BaCrO_4 and SrCrO_4 as being complete.
- 832.** What is the range of $[\text{SO}_4^{-2}]$ for the selective precipitation of PbSO_4 in the presence of Ca^{+2} ? The concentration of the cations is 0.25 *M*. The solubility of PbSO_4 is 3.11×10^{-2} g./l., and the solubility of CaSO_4 is 1.02 g./l. Assume complete ionization of PbSO_4 and CaSO_4 .
- 833.** A solution is known to contain 10 cc. of 0.5 *N* MgCl_2 in 50 cc. Assume the ionization of the MgCl_2 as 70 per cent. The solubility product

- $[\text{Mg}^{+2}] \times [\text{OH}^{-}]^2 = 3.6 \times 10^{-11}$. Calculate the minimum $[\text{OH}^{-}]$ that will start precipitation of $\text{Mg}(\text{OH})_2$.
- 834.** A solution contains 200 mg. of magnesium chloride is 50 cc. Assume the ionization of the MgCl_2 as 70 per cent. The solubility product $[\text{Mg}^{+2}] \times [\text{OH}^{-}]^2 = 3.6 \times 10^{-11}$. Calculate the minimum $[\text{OH}^{-}]$ that will start precipitation of $\text{Mg}(\text{OH})_2$.
- 835.** The solubility of barium chromate is 0.0037 g./l. at 20°C . Given a solution that contains 200 mg. of barium acetate to which is added 0.5 cc. of 0.2 *N* K_2CrO_4 , the volume measuring 100 cc. The potassium chromate is ionized to the extent of 80 per cent. Calculate (a) the solubility product $[\text{Ba}^{+2}] \times [\text{CrO}_4^{-2}]$; (b) the weight of barium chromate that remains in solution.
- 836.** The solubility of strontium chromate is 1.2 g./l. at 20°C . Given a solution that contains 200 mg. of strontium acetate to which is added 0.5 cc. of 0.2 *N* K_2CrO_4 , the volume measuring 100 cc. The potassium chromate is ionized to the extent of 80 per cent. Calculate (a) the solubility product $[\text{Sr}^{+2}] \times [\text{CrO}_4^{-2}]$; (b) the weight of strontium chromate that will remain in solution.
- 837.** A solution, acidified with hydrochloric acid and containing 200 mg. of lead chloride in 100 cc., is saturated with hydrogen sulfide, at room temperature and atmospheric pressure. Under these conditions, it was found that 0.0001 g. of PbCl_2 escaped precipitation with H_2S . The hydrochloric acid is 12 *N*. Assume the ionization of this hydrochloric acid solution to be 90 per cent. S.P.C. of $\text{PbS} = 3.4 \times 10^{-28}$. Calculate the number of cubic centimeters of hydrochloric acid, of the foregoing normality, that must have been present in the solution.
- 838.** In a laboratory experiment 0.75 g. of lead chloride was dissolved in 1 l. of 1.2 *N* HCl , and the solution placed in a large flask in a thermostat at 25°C . This solution was then saturated with H_2S at atmospheric pressure. At this temperature and pressure the saturation value of H_2S is such that $[\text{H}^{+}]^2 \times [\text{S}^{-2}] = 1.1 \times 10^{-23}$. The hydrochloric acid is ionized in this solution to the extent of 73.4 per cent. The precipitate of PbS obtained under these conditions was then filtered out. The filtrate was made ammoniacal, and H_2S passed into this solution. The $(\text{NH}_4)_2\text{S}$ thus produced precipitated practically all the Pb^{+2} that escaped in the first process with H_2S . This precipitate was next filtered out and converted, first, into $\text{Pb}(\text{NO}_3)_2$ and, then, to PbSO_4 which was dried and weighed. It was found, by calculation, that 9.65×10^{-3} g. of lead chloride had escaped precipitation in the first process with H_2S . From these data, calculate the S.P.C. of PbS .
- 839.** Determine the $[\text{H}^{+}]$ in a 0.3 *N* NH_4OH solution. The $K_{\text{ionization}}$ for NH_4OH is 1.8×10^{-5} ; $K_{(\text{H}_2\text{O})}$ is 1×10^{-14} .
- 840.** Determine the $[\text{OH}^{-}]$ in a 0.01 *N* $\text{HC}_2\text{H}_3\text{O}_2$ solution. The $K_{\text{ionization}}$ for $\text{HC}_2\text{H}_3\text{O}_2$ is 1.8×10^{-5} ; $K_{(\text{H}_2\text{O})}$ is 1×10^{-14} .
- 841.** The $K_{\text{ionisation}}$ for HCN is 7×10^{-10} , and $K_{(\text{H}_2\text{O})}$ is 1.1×10^{-14} . Determine (a) the $K_{\text{hydrolysis}}$ for 0.1 *M* KCN solution and (b) the $[\text{OH}^{-}]$ in this solution.

- 842.** The $K_{\text{ionization}}$ for HNO_2 is 5×10^{-4} , and $K_{(\text{H}_2\text{O})}$ is 1.1×10^{-14} . Determine (a) the $K_{\text{hydrolysis}}$ for 0.1 M KNO_2 solution and (b) the $[\text{OH}^-]$ in this solution.
- 843.** Determine the percentage of hydrolysis of (a) 0.01 M ; (b) M NaNO_2 solutions. The $K_{\text{ionization}}$ for HNO_2 is 5×10^{-4} , and $K_{(\text{H}_2\text{O})}$ is 1×10^{-14} .
- 844.** Calculate the percentage of hydrolysis of (a) M ; (b) 0.01 M KCN solutions. The $K_{\text{ionization}}$ for HCN is 7×10^{-10} , and $K_{(\text{H}_2\text{O})}$ is 1×10^{-14} .
- 845.** What is the $[\text{OH}^-]$ in a 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ solution that is 1.3 per cent ionized? $K_{(\text{H}_2\text{O})}$ is 1.1×10^{-14} .

APPENDIX

TABLE I.—CONVERSION FACTORS FOR WEIGHTS AND MEASURES

NOTE.—For a more extensive table of conversion factors, the reader is referred to Lange's "Handbook of Chemistry."

<i>To convert from</i>	<i>To</i>	<i>Multiply by</i>
Acres (U. S.)	square feet	43,560
Acres (U. S.)	square meters	4,046.873
Acres (U. S.)	square rods	160
Acres (U. S.)	square yards	4,840
Angstrom units	inches	3.937×10^{-9}
Angstrom units	meters	1×10^{-10}
Atmospheres	inches of Hg at 32°F.	29.921
Atmospheres	grams per square centimeter	1,033.3
Atmospheres	millimeter of Hg	760
Atmospheres	pounds per square inch	14.696
Barrels, cement	pounds of cement	376
Barrels, oil	gallons (U. S.)	42
Barrels (U. S., dry)	bushels	3.281
Barrels (U. S., dry)	cubic inches	7,056
Barrels (U. S., liquid)	gallons	31.5
Board-feet	cubic inches	144
B.t.u.	calories (small)	252
Bushels (U. S., dry)	cubic feet	1.2444
Bushels (U. S., dry)	liters	35.238329
Bushels (U. S., dry)	quarts (dry)	32
Calories (large)	B.t.u.	3.968
Centimeters	angstrom units	1×10^8
Centimeters	inches (U. S.)	0.39370
Centimeter of mercury at 0°C.	pounds per square inch	0.19337
Cords	cubic feet	128
Cords	cubic meters	3.625
Cubic centimeter	cubic inches	0.061023
Cubic centimeter	gallons (British)	2.1997×10^{-4}
Cubic centimeter	gallons (U. S.)	2.6417×10^{-4}
Cubic centimeter	ounces (U. S., fluid)	0.033814
Cubic centimeter	pints (U. S., liquid)	0.0021134
Cubic centimeter	quarts (U. S., dry)	9.0808×10^{-4}
Cubic centimeter	quarts (U. S., liquid)	0.0010567
Cubic feet (U. S.)	board feet	12
Cubic feet (U. S.)	bushels (U. S.)	0.80357

<i>To convert from</i>	<i>To</i>	<i>Multiply by</i>
Cubic feet (U. S.)	cubic centimeters	28,317
Cubic feet (U. S.)	cubic inches	1,728
Cubic feet (U. S.)	cubic yards	0.037037
Cubic feet (U. S.)	gallons (British)	6.229
Cubic feet (U. S.)	gallons (U. S.)	7.481
Cubic feet (U. S.)	liters	28.316
Cubic feet (U. S.)	quarts (U. S., dry)	25.714
Cubic feet (U. S.)	quarts (U. S., liquid)	29.922
Cubic feet of water (60°F.)	pounds	62.37
Cubic inches (U. S.)	cubic centimeters	16.387162
Cubic inches (U. S.)	cubic meters	1.63871×10^{-6}
Cubic inches (U. S.)	gallons (U. S.)	0.0043290
Cubic inches (U. S.)	liters	0.0163868
Cubic inches (U. S.)	ounces (fluid) (U. S.)	0.5541
Cubic inches (U. S.)	quarts (U. S., liquid)	0.017316
Cubic meters	cubic feet (U. S.)	35.314445
Cubic meters	cubic inches	61,023
Cubic meters	gallons (U. S.)	264.173
Feet (U. S.)	centimeters	30.480
Gallons (U. S.)	cubic centimeters	3,785.4
Gallons (U. S.)	cubic feet	0.13368
Gallons (U. S.)	cubic inches	231
Gallons (U. S.)	gallons (British)	0.83268
Gallons (U. S.)	liters	3.78533
Gallons (U. S.)	ounces (U. S., fluid)	128
Gallons (U. S.)	pounds (avoir.) of water at 62°F. (16.7°C.)	8.3378
Grains	milligrams	64.7989
Grains	ounces (avoir.)	0.0022857
Grams	grains	15.4324
Grams	milligrams	1,000
Grams	ounces (avoir.)	0.0352739
Inches (U. S.)	centimeters	2.54
Kilograms	ounces (avoir.)	35.2739
Kilograms	pounds (avoir.)	2.204622
Liters	cubic feet	0.035316
Liters	cubic inches	61.025
Liters	gallons (British)	0.219976
Liters	gallons (U. S.)	0.2641776
Liters	ounces (U. S., fluid)	33.8143
Liters	quarts (U. S., liquid)	1.0566818
Meters	feet (U. S.)	3.28083
Meters	inches (U. S.)	39.3700
Meters	rods (U. S.)	0.198838
Meters	yards (U. S.)	1.093611
Microns	millimeters	0.001

<i>To convert from</i>	<i>To</i>	<i>Multiply by</i>
Microns	millimicrons	1,000
Miles (U. S., statute)	feet	5,280
Miles (U. S., statute)	kilometers	1.609347
Miles (U. S., statute)	rods	320
Milligrams	grains	0.015432
Milligrams	grams	0.001
Milliliters	cubic centimeters	1.000027
Milliliters	cubic inches	0.061025
Milliliters	liters	0.001
Milliliters	minims (U. S.)	16.2311
Milliliters	ounces (U. S., fluid)	0.0338147
Millimeters	centimeters	0.1
Millimeters	inches (U. S.)	0.039370
Millimeters	meters	0.001
Millimeters	microns	1,000
Millimeters of Hg at 0°C.	atmospheres	0.00131579
Millimeters of Hg at 0°C.	grams per square centimeter	1.3595
Millimeters of Hg at 0°C.	kilograms per square meter	13.595
Millimeters of Hg at 0°C.	pounds per square foot	2.7845
Millimeters of Hg at 0°C.	pounds per square inch	0.019337
Millimicrons	angstrom units	10
Millimicrons	centimeters	1×10^{-7}
Millimicrons	microns	0.001
Ounces (avoirdupois)	drams (avoirdupois)	16
Ounces (avoir.)	drams (Troy or apoth.)	7.29166
Ounces (avoir.)	grains	437.5
Ounces (avoir.)	grams	28.349527
Ounces (avoir.)	ounces (Troy or apoth.)	0.9114583
Ounces (avoir.)	pounds (avoir.)	$\frac{1}{16}$
Ounces (avoir.)	pounds (Troy)	0.0759548
Ounces (Troy or apoth.)	drams (avoir.)	17.55428
Ounces (Troy or apoth.)	drams (Troy or apoth.)	8
Ounces (Troy or apoth.)	grains	480
Ounces (Troy or apoth.)	grams	31.103481
Ounces (Troy or apoth.)	milligrams	31,103.481
Ounces (Troy or apoth.)	ounces (avoir.)	1.09714
Ounces (Troy or apoth.)	pounds (avoir.)	0.068571
Ounces (U. S., fluid)	cubic centimeters	29.5737
Ounces (U. S., fluid)	cubic inches	1.80469
Ounces (U. S., fluid)	drams (fluid)	8
Ounces (U. S., fluid)	gallons (U. S.)	$\frac{1}{128}$
Ounces (U. S., fluid)	liters	0.0295729
Ounces (U. S., fluid)	milliliters	29.5729
Ounces (U. S., fluid)	pints (U. S., liquid)	$\frac{1}{16}$
Ounces (U. S., fluid)	quarts (U. S., liquid)	0.03125
Paces	feet	2.5

<i>To convert from</i>	<i>To</i>	<i>Multiply by</i>
Paces	inches	30
Parts per million	grains per gallon (U. S.)	0.0584
Parts per million	pounds per million gallons (U. S.)	8.345
Pecks (U. S.)	bushels	0.25
Pecks (U. S.)	cubic inches	69.365
Pecks (U. S.)	liters	8.80958
Pecks (U. S.)	pints (dry)	16
Pounds (avoir.)	drams (avoir.)	256
Pounds (avoir.)	grains	7,000
Pounds (avoir.)	grams	453.592427
Pounds (avoir.)	ounces (avoir.)	16
Pounds (avoir.)	ounces (Troy)	14.5833
Pounds (Troy)	grams	373.2418
Pounds (Troy)	ounces (Troy)	12
Pounds (Troy)	pounds (avoir.)	0.822857
Quarts (U. S., liquid)	cubic centimeters	946.358
Quarts (U. S., liquid)	cubic inches	57.749
Quarts (U. S., liquid)	liters	0.946333
Quarts (U. S., liquid)	ounces (fluid, U. S.)	32
Radians	degrees	57.29578
Reams	sheets	480
Rods (surveyor's measure)	feet	16.5
Tons (long)	pounds (avoir.)	2,240
Tons (metric)	kilograms	1,000
Tons (short)	pounds (avoir.)	2,000
Yards (U. S.)	centimeters	91.440183

This table of conversion factors for weights and measures is compiled from Lange's "Handbook of Chemistry." Special permission to reproduce it has been granted by the publishers, Handbook Publishers, Inc., Sandusky, Ohio.

TABLE II.—DENSITY OF GASES

Gas	Form- ula	Grams per liter at 0°C., 760 mm.	Gas	Form- ula	Grams per liter at 0°C., 760 mm.
Air.....	1.2929	Hydrogen.....	H ₂	0.08987
Acetylene.....	C ₂ H ₂	1.1731	Hydrogen sulfide..	H ₂ S	1.5392
Ammonia.....	NH ₃	0.7710	Krypton.....	Kr	3.708
Argon.....	A	1.7832	Methane.....	CH ₄	0.7168
Bromine.....	Br ₂	7.1388	Neon.....	Ne	0.9002
Butane, iso.....	C ₄ H ₁₀	2.6738	Nitrogen.....	N ₂	1.2505
Carbon dioxide...	CO ₂	1.9769	Nitric oxide.....	NO	1.3402
Carbon monoxide..	CO	1.2504	Nitrous oxide.....	N ₂ O	1.9778
Chlorine.....	Cl ₂	3.214	Oxygen.....	O ₂	1.4290
Ethane.....	C ₂ H ₆	1.3566	Phosphine.....	PH ₃	1.5294
Ethylenè.....	C ₂ H ₄	1.2604	Propane.....	C ₃ H ₈	2.0200
Helium.....	He	0.1784	Silicon tetrafluoride	SiF ₄	4.684
Hydrofluoric acid..	H ₂ F ₂	0.894	Sulfur dioxide.....	SO ₂	2.9269
Hydrobromic acid..	HBr	3.6445	Steam at 100°C....	0.581
Hydrochloric acid..	HCl	1.6392	Xenon.....	Xe	5.851

Compiled from Smithsonian Tables (1914) and Landolt-Börnstein-Roth-Scheel's "Physikalische-chemische Tabellen," 1923.

TABLE III.—DENSITY AND VOLUME OF WATER

The mass of 1 cc. at 4°C. is taken as unity

Temp., °C.	Density	Volume
-10°	0.9981	1.0018
- 5°	0.9993	1.0007
0°	0.9998	1.0001
4°	1.0000	1.0000
5°	0.99999	1.00001
10°	0.99973	1.00027
15°	0.9991	1.0008
20°	0.9982	1.0017
25°	0.9970	1.0029
30°	0.9956	1.0043
35°	0.9940	1.0059
40°	0.9922	1.0078
45°	0.9902	1.0098
50°	0.9880	1.0120
55°	0.9837	1.0144
80°	0.9718	1.0289
90°	0.9653	1.0359
100°	0.9583	1.0434
110°	0.9510	1.0515

Compiled from Smithsonian Tables (1914).

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